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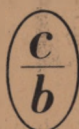
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LITHOLOGY AND MINERAL RESOURCES

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A translation of *Litologiya i Poleznye Iskopaemye*

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to have taken place reasonably soon thereafter.*

The phenomenon of sand diapirism is studied, which is associated with mud volcanoes of the Cheleken Peninsula; the elissional mechanism of formation of mud volcanoes, abnormally high stratal pressures (AHSP), and oil and gas deposits is proved.

Diapirism processes are usually identified as the extrusion of plastic sedimentary rocks, such as rock salt, gypsum, clays, clay shales, and others by tectonic stresses. In the normal state, sand and sandstone are not plastic formations; in some rare settings, however, their fluidity may be increased. Quicksand develops in sand beds, layer ruptures arise, and "clastic" or sand dikes and slumps are likely to occur [35].

In earlier publications we have discussed at length the mechanism of this phenomenon and the conditions favorable to sand diapirism in the Paleogene-Neogene beds of the Caucasus [46, 47, 49, 50].

Studies of mud volcanoes by the authors in 1982-1983 in Azerbaidzhan, the Southern Caspian region, and Western Turkmenia have established a close genetic correlation between sand diapirism and mud volcanoes; it is also the subject of the present paper.

Geologically, Cheleken Peninsula makes up part of the West Turkmenian depression. It includes a gently sloping plane gradually descending from the Greater Balkhan and the Kopetdag to the Caspian Sea; it is compounded by the Chokhrak upland. Tectonically, the central part of Cheleken is a large anticlinal northeasterly fold of a complex structure.

At the core of the Cheleken fold, Pliocene red sediments are exposed, overlain by Akchagyl and Apsheron strata; the sides of the structure are formed of post-Pliocene sediments of Baku, Khazarian, Khvalynian, Neocaspian stages.

The red bed exhibits alternating calcareous brown, red, or red-brown clay with interlayers of obliquely laminated sandstone and siltstone. Washout surfaces are frequent, with rolling stones and numerous riverbed incisions. The bed probably belongs to the facies of a submerged delta of the ancient Uzboi River and was formed in extremely shallow settings. It is 2500-2600 m thick.

The Akchagyl bed is formed of gray-greenish calcareous sheet clays containing several interlayers of white volcanic ash; phosphatized fish remains are abundant, reflecting a marine origin. The thickness varies from 20 to 30 m.

The Apsheron strata are composed of gray and brownish-gray sandy clays, interstratified with marker beds of coquina, sand, and volcanic ash. Mud volcano breccia beds are especially common at the center of the peninsula. The Apsheron strata are 260-280 m thick.

The Baku stage begins with a bed of gastropod limestone-coquina, overlain by greenish-gray and pink clays with sand and siltstone interlayers. The profile is topped by black clays. Submarine-landslide structures are widespread. The thickness is 180-250 m.

The Khazarian layers are represented by shell limestone, consisting of *Corbicula fluminalis* Mull. and black clays. The strata are 35 m thick.

The Khvalynian sediments consist of poorly sorted sands with a ferruginous conglomerate found at their base. They are 20 m thick.

The Neocaspian stage, which completes the normal stratigraphic profile of the region, is represented by yellowish-gray sandstone forming beaches, barchans, and dunes.

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The Cheleken fold is a large brachyanticline 35 km long and 15 km wide; its elevation amplitude relative to the adjacent depressions is 1700 m.

In its central part the fold is cut across by a large number of disruptive faults, likened after Andrusov, [2] to a broken plate. Downthrows of two systems stand out amid the general mass of faults.

The first system of downthrows is traceable in a sublatitudinal or northeasterly direction, more or less parallel to the upland axis; the second system is developed in the western part of the fold and is characterized by a northwesterly course of the faults.

At the intersection of the faults of these two directions are the active mud volcanoes Western Porsugel and Pink Porsugel and ancient Aligul mud volcano.

The area of Aligul is a complex tectonic node located close to the center of the tectonic structure (Fig. 1). The Aligul stow is bounded on the west by a submeridional Aligul-Kurtepe downthrow, at which the red bed is in contact with the field of Akchagyl rocks and mud breccias of the ancient volcano.

A sublatitudinal Kurtepe downthrow is traceable in the north; red rocks come into contact here with Akchagyl and Apsheron layers.

At the middle of the Aligul stow a plateau upland is situated, which is cut by ravines on all sides; it is formed of mud breccias, appearing in plan as a pentagon bounded on all sides by intersecting faults. South of the mud breccia spot, greenish-gray clays, sands, and marlstones of the Baku stage are found in a submeridional valley; in the southwest, the Aligul-Kurtepe downthrow separates them from the zone of the Khazarian shell limestone and black clay; in the east, the valley is confined by an arc-shaped system of faults with "Paleogene rock masses" and mud breccias contained in the system.

The structure of the Aligul mass has been the subject of numerous studies.

Ivanov [20], one of the early investigators of the geology of Cheleken, believed the Aligul mass to be an accumulation of mud breccias of a submarine mud volcano that had been active since the Apsheron age. Andrusov [3] noted later, quoting from Ivanov's letter of February 23, 1917, that the latter had proved that there are no peripheral downthrows or even small fissures bounding Aligul in the west, north, or east, and that there is only one semicircular crack up to 7 m wide through which "slurry" had effused; by "slurry" Ivanov referred to fossil volcanocoe. A clastic dike was apparently described near this large fault [20].

In the mud breccia bed forming the Aligul mass, Ivanov discerned "olive and greenish sandstones" forming large blocks up to several meters in size masked by mud volcano ooze. In addition, near the mud volcano he discovered yellow limestone masses with abundant Mesozoic fauna, measuring up to 10 m³; these block boulders are currently found in rocks of different age but are obviously ejections from older volcanic eruptions.

Ivanov [20] was the first to notice numerous interlayers of mud volcano breccia in Apsheron rocks near the Aligul volcano, varying in thickness from 0.2 to 11 m; with the distance from this area the breccias beds wedge out and gradually are succeeded by black unswelling clays. Andrusov shared this interpretation [3].

Later, Kalitskii and Weber [9, 22], who thoroughly mapped the entire Cheleken area, offered a different theory of the structure of the Aligul stow. These authors believed the principal structure to be a "'horst' bounded polygonally by downthrows and exhibiting soft Paleogene rocks exposed nowhere on the island except for this site" [9, p. 120]. South of this horst, a large heavily distorted graben is situated in which Khazarian deposits are widespread (layers with *Corbicula fluminalis*). These investigators believed that "Aligul horst is most remarkable tectonically; it is thrust upward to at least 400 sazhen.* Inexplicably, this motion affected little the neighboring rocks" [9, p. 120].

The vent of the Aligul mud volcano was placed by Kalitskii to the west of the horst consisting of Paleogene rocks; here he found protrusions represented by blocks of different rocks (from Jurassic limestone to Paleogene sandstone) and faults filled with mud volcano breccia.

Porfir'ev [36] prepared a geological description and a map of the Aligul area. This investigator rejected the hypothesis of a horst structure of the central field and joined

*Translator's Note: 1 sazhen = 2.138 m.

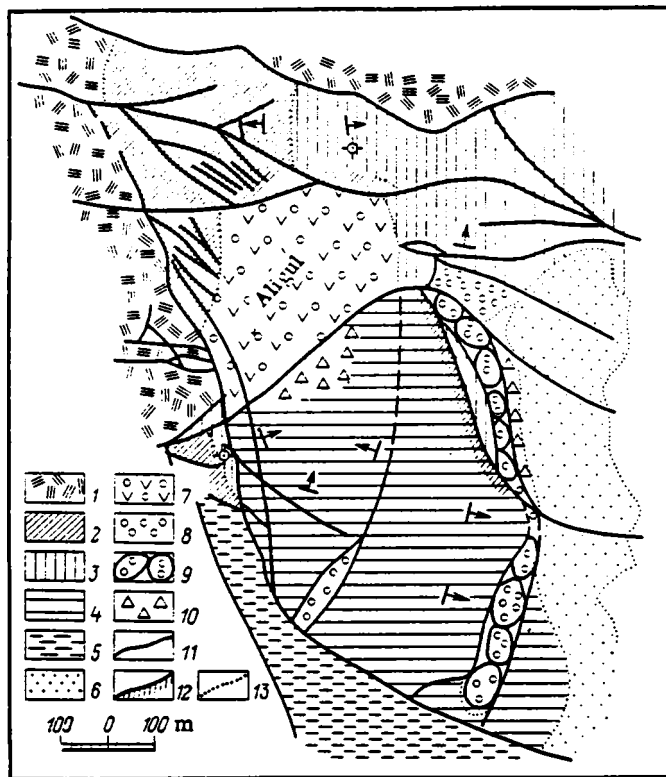


Fig. 1. Geological structure of the area of the Aligul mud volcano (Cheleken Peninsula): (1) red bed; (2-5) layers (2 - Akchagyl, 3 - Apsheron, 4 - Baku, 5 - Khazarian); (6) Quaternary; (7-8) mud breccias (7 - neck volcano facies, 8 - peripheral facies occurring amid normal marine sediments); (9) diapiric breccia blocks; (10) redeposited fragments of mud breccias; (11) faults; (12) ferruginated faults; (13) normal geological rock contacts.

Ivanov and Andrusov in the belief that "the Aligul table mountain is a part of an extensive cover of mud volcano breccia deposited in the middle section of the Apsheron stage" [36, p. 6]. He also believed that the volcano's main neck should be somewhere in the center of the bed, because small gas necks in the development field of Akchagyl rocks could hardly be the ducts for eruption of huge separated Paleogene blocks.

Porfir'ev did not discover Ivanov's "semicircular crack" "through which slurry was effused," but emphasized the brachysynclinal structure of the field of Khazarian rocks, which, occurring with a gentle tilt at the core of the structure, subside at an angle of 80° on the eastern side bounded by the downthrow.

In 1952-53 Semenovich [40, 41] conducted structural-mapping drilling near the Aligul stow, which established that the massif of mud breccia and Paleogene boulders is not a pierced kernel but a cover normally occurring in the west over Akchagyl sediments and in the east over Apsheron beds; in the north and south it is truncated by sublatitudinal downthrows. The cover of Paleogene rock, boulders, and mud breccia hides the main neck of the mud volcano situated somewhere at the center of the massif.

A profile section across the Aligul massif and the structural map of the region compiled by Semenovich [41] clearly reveal traces of sagging within the cover of boulders and mud breccias; this correlates with the structure of the Khazarian syncline, conjugated in the southeast with the cover and surrounded by circular faults.

Semenovich concluded that the eruptions of Aligul mud volcano started in the Lower Apsheron and continued until the Khazarian time; they began with the ejection of large boulders and blocks of Paleogene rocks followed by effusion of mud breccia. These alternated with normal sedimentation in marine and lacustrine basins; eruptions were completed by the sagging near Aligul massif, compensating the outpouring of large amounts of mud breccia from the

earth's interior. A depression funnel was apparently formed at the site of the volcano with a lake in it, and for some time it was similar morphologically to the Western and Pink Porcupines.

The subsequent extinction of mud activity, the rise of the region, and the erosion of much of the young deposits completed the lacustrine stage and exposed the roots of the mud volcano cover.

Near Aligul stow (see Fig. 1) are several segments, which can be interpreted as additional channels through which the eruptive material was brought to the day surface, as well as the principal neck of the mud volcano, hidden under the burden of mud breccias and Paleogene blocks. For example, west of the Aligul mass within the occurrence field of Akchagyl deposits, mud breccias are widespread amid numerous cracks and faults; above one of the faults, cones composed of Paleogene rock fragments cemented by a clay mass have been preserved.

In the southern part of the Khazarian syncline, remnants of sandstones 0.5-1.5 m thick are exposed; they form a lens-shaped body traceable for 7-10 m along the course of the fault.

Of most interest genetically is the phenomenon observed in the eastern part of the Khazarian syncline along circular faults limiting this tectonic structure (see Fig. 1).

Here, one observes a ridge of blocks of gray carbonate sandstones and dark brown chertolites (bituminous micaceous clay sandstones) enclosed between two faults. The ridge is 5 to 9 m wide, of a variable width, and can be traced from the Aligul massif to the south along the entire Khazarian brachysyncline over 700-800 m (Figs. 2a and 3a).

Within the ridge, which rises over the area south of Aligul massif, blocklike portions with prevalent gray sandstones and areas of widespread dark-brown clay sandstones occur in a peculiar pattern with patches measuring 2-3 m.

Clay sandstones under the microscope are seen to consist of angular, less often rounded, fragments of quartz, feldspar, chalcedony, hornblende, with muscovite, sericite, and numerous carbonate complex grains. They vary in size from 0.005 to 0.15 m. The rock is cemented by a clay mass locally pigmented with brownish-gray bitumoids. An indistinct stratification is typical, which on the bedding plane often gives way to a flow structure (see Fig. 3b). The rock is remarkably similar to clayey mud breccias widespread within the Aligul massif itself.

Gray carbonate sandstones within the outcrop studied by us are also frequent. They are represented by fragments of quartz, chalcedony, feldspars (microcline and orthoclase), hornblende, muscovite, and sericite, which are angular; coarse-grained fractions are predominant. The rock is usually cemented with coarse-crystalline calcite; locally, a corrosion of quartz fragments, substitution of carbonates for hornblende and feldspar, and pyritization of iron-containing minerals are observed.

Dark-brown clayey and gray carbonate sandstones in the outcrops enter in complex structural interrelationships. Gray sandstones occur more often in subordinate amounts, forming nodulelike bodies, blocks, and blocklike formations, pipe and pipelike inclusions, and, finally, sandy clastic dikes (Fig. 4).

Nodulelike bodies are usually widespread; they vary in diameter from 2 to 20 cm. Nodular formations of an almost perfect spherical shape occur sometimes, but next to them one finds stick-shaped, spindlelike, or cake-shaped sand bodies included in dark-brown chertolite. Rounded sand bodies sometimes merge into double, triple, or grapelike accumulations, forming inclusions of a peculiar appearance (see Fig. 4a). As is clear from photographs (Fig. 5), the morphological outlines of these nodular bodies are difficult to represent in a drawing; these formations easily make transitions to boulders and pipes. Accumulations of liquid bitumoids are often found within such nodules.

Blocklike bodies made of gray carbonate sandstones sometimes measure 10-15 cm across, although in some the diameter reaches 2-4 m. Some of the morphological features of these blocks are illustrated by Fig. 3a; their typical shapes are shown in Fig. 4b, c. Bodies with a crescent cross section (roll-like) or structures of a snowball type (twists) occur infrequently amid the blocklike sandstone units.

The long axes of the blocks are sometimes oriented perpendicular to bedding, constituting pipelike bodies.

Pipelike inclusions sharply predominate in the northern part of the exposure adjacent to the Aligul massif; they endow the sand mountain between the two faults with its unique appear-

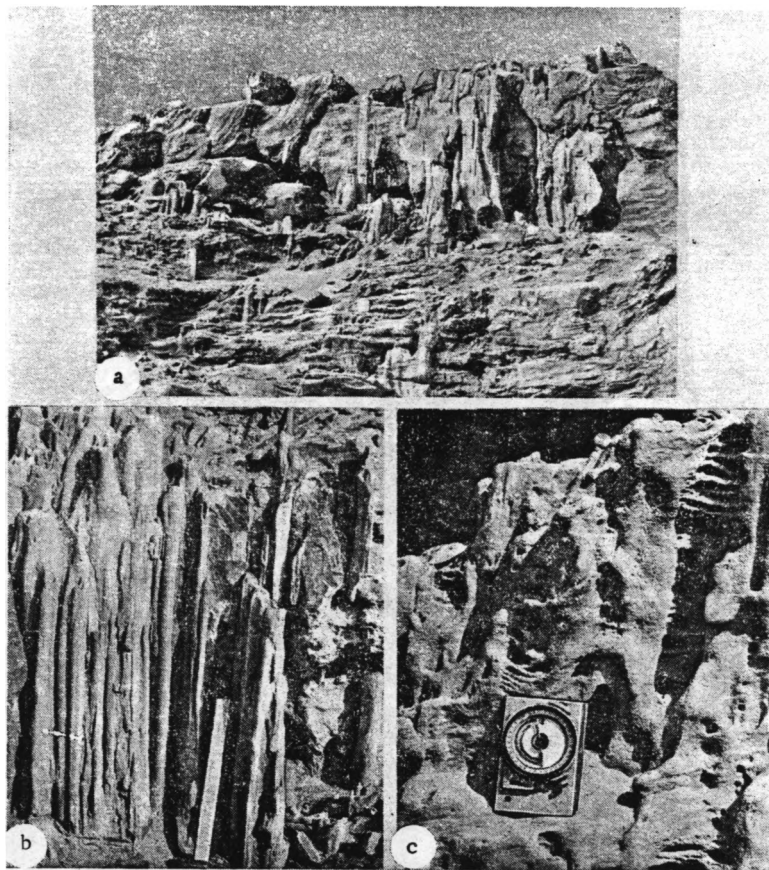


Fig. 2. Sand diapiric breccias: a) general diapirs of the exposure site (dark areas are brown clay sandstones—chlidolites impregnated with a bitumoid; gray areas are gray carbonate sandstones); b) a detail of the exposure: organlike accumulations of sand pipes; c) structures on the surface of carbonate sandstones.

ance (see Fig. 2a). The pipeline bodies vary in size from 1 to 30 cm thick and 10 cm to 0.9 m long. Single pipes are sometimes found, but they are mostly grouped as sets reminiscent of an organ, as it were, piercing through crumpled mass of dark brown clay sandstones (see Figs. 2b and 4c). The peripheral portion of a sand pipe is usually cemented more strongly in its center; in the course of weathering sand was more easily removed from the inner cavity, forming a real pipe. Smears and even liquid bitumoid inclusions are often found within such formations. The weathering of sets of pipelike bodies in certain areas resulted in peculiar latticelike structures (see Fig. 2c).

Clastic or sand dikes occur more locally; we have found them approximately in the middle of the exposure 300–400 m south of Aligul massif at the site where an outcrop of block sandstones is cut across by the fault (see Fig. 1).

On a leveled surface of exposed Khazarian layers dipping west at $75-80^\circ$, two large clastic dikes are distinctly seen, which have been processed heavily by deflation; they branch off from large blocks of gray carbonate sandstone and wedge out from east to west over a stretch of 22–25 m.

The morphological features of one of these clastic dikes can be seen in Fig. 4d; it is a variety of Z-shaped dikes compounded by elbow-shaped bends. The dike is 0.25 m thick and 24 m long. It consists of white high-carbonate sandstone; under the microscope large round inclusions of clay rocks are seen amid fragments of quartz, feldspar, hornblende, and mica, immersed in fine-grained carbonate matrix. The clay inclusions are usually three to four times as large as fragments of terrigenous minerals and surrounded by a coarse crystalline crustification carbonate fringe. In the middle of the exposure the dike cuts across a silted sandstone bed. In all the other areas it is found amid clays.

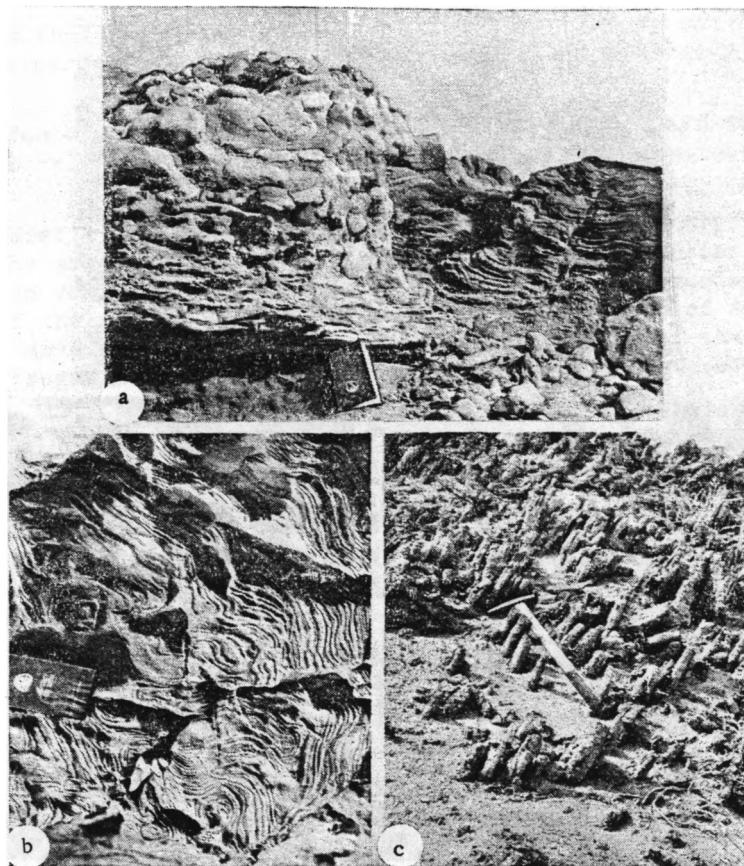


Fig. 3. Sand diapiric breccias: a) general view of the exposure site (dark areas are brown clay sandstone impregnated with a bitumoid; gray areas are gray carbonate sandstones); b) flow structures on the surface of brown clay sandstones; c) sand pipes cemented with gypsum and iron hydroxides.

A large number of smaller tectonic cracks filled with carbonate sandstone have been found close to dikes.

In general, the block formation consisting of a complex pattern of cooccurrence of dark-brown clay sandstones and gray calcareous sandstone structures, described earlier, is enclosed between two large faults surrounding the Khazarian syncline in a semicircle; this formation appears to be the "crack" of Ivanov [20] through which "slurry" was effused to the day surface. By its formation mechanism it is a typical "horizon with inclusions" or ancient quicksand whose genesis may be attributed to two circumstances.

First of all, both components, i.e., sand diluted with clay-bitumoid fluid and sand diluted by water with carbon dioxide, were moved by a strong pressure through a system of faults and initially behaved as two viscous substances. The ratios of the structures indicate that the more liquefied (i.e., less viscous) sandstone with water and carbon dioxide formed in the sand with clayey-bitumoid fluid contain isolates of a complex morphology resembling bubbles, blocks, or pipes.

Secondly, it is certain that sand diluted with carbon dioxide could be fixed in such shapes only if it solidified instantly, turned into hard sandstone from viscous and semiliquid sand.

The mechanism of such a rapid solidification of quicksand has been discussed by us in an earlier study with special reference to clastic sand dikes common in the Middle Eocene of the eastern Ciscaucasian region [46, 47, 50]. We demonstrated that dikes are typical injections of a semiliquid sand pulp into solid preformed beds of less plastic clay. Quicksand units (bodies of liquified sand), were formed as sand beds subsided to large depths and some fluid

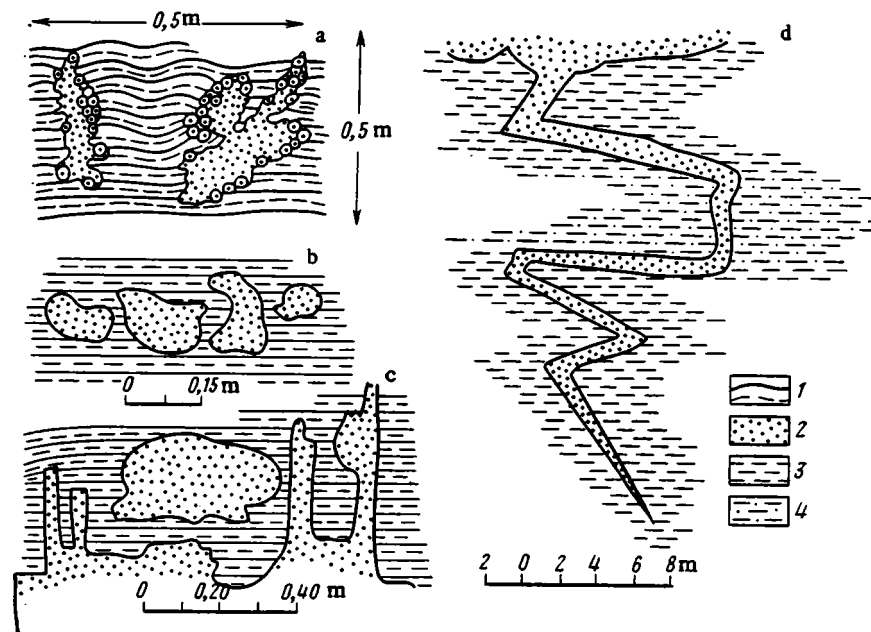


Fig. 4. Drawings of structural relationships of diapiric breccia rocks: a) grapeli-like accumulations of nodular bodies of carbonate sandstone in brown clayey chlidolites; b) blocklike sandstone body shapes; c) blocks and pipes of gray sandstones; d) a clastic dike in Khazarian sediments.

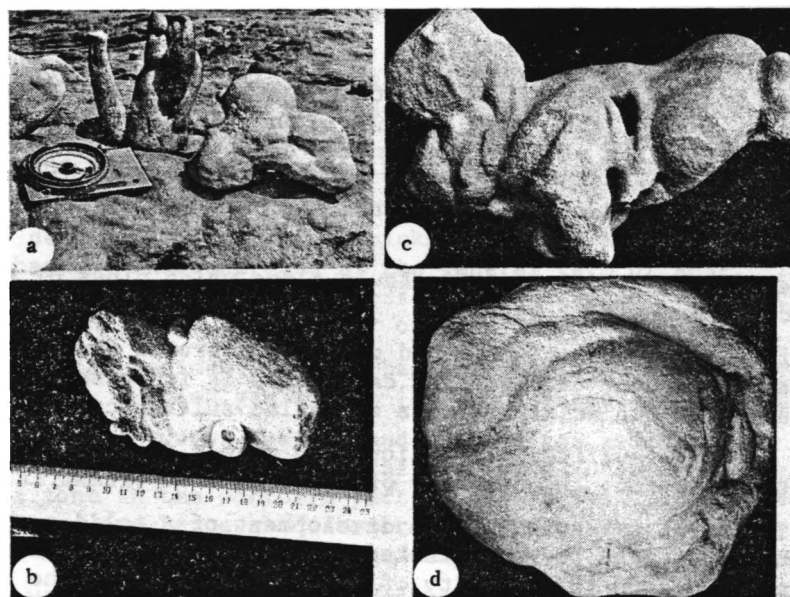


Fig. 5. A photograph of pipe-shaped (a), blocklike (b, c), and nodulelike (d) bodies composed of gray carbonate sandstone.

that liquefied them was supplied into them under pressure. The tremendous internal stratal pressures in the sand bed in certain areas, could exceed the geostatic pressure. the cohesion of quartz fragments was reduced, and a sand bed for a period of time was transformed into a typical quicksand. In some portions of the basin its plastic properties began to exceed substantially the plastic properties of the enclosing clays.

In the specific conditions of deep catagenesis zones in which liquefied sands and dense hardened clays came into close contact, any disjunctive disruption of separating clays and, of course, a separation crack with a typical internal vacuum, would result in an intrusion of a semiliquid sand pulp into the cavity.

The development of a clastic dike was reminiscent of a pneumatic crack; it occurred instantly, increasing the volume of the sand bed and thus reducing stratal pressure. The drop of the stratal pressure again equilibrated the system, and the sand returned to its low-plasticity condition. The intrusion of a quicksand unit into the crack was associated with a mechanical separation and capture of angular fragments of clay nodules and other protrusions from the crack walls.

The stratal pressure drop was conducive to a decline of carbon dioxide pressure, which in turn led to a precipitation of solid carbonate from the fluid, which cemented the dike body. Quicksand thus, as it intruded into the crack, was resolidified not only because of the recovery of cohesion of mineral fragments but also as they were densely connected by carbonate authigenic minerals — the neomorphs.

Interpolating this process to other forms of sandstone carbonatization, one can assume that their rapid solidification was caused by the degassing of fluids that liquefied sand near the day surface.

Along with the carbonatization of sandstones, they were intensely sulfidized locally along the faults.

Indeed, at a distance of 2–3 m to the west of the crack filled with carbonate-clay sandstones in the same area near Aligul, another tectonic fault is clearly traced by relatively large protrusions (see Fig. 3c).

The surface of these mounds is covered by what looks like a forest of pipes, ranging in size from 1×10 cm to 4×40 cm. Mostly the pipes as single units rise from ferruginous soil cover, but sometimes merge into a brushlike formation, hiding the soil completely.

A detailed analysis of the pipes has shown that they are made of sandstone; as in some of the instances described earlier, the sandstone consists of angular and poorly rounded fragments of quartz, plagioclase, clay rocks, less often mica (muscovite), and strongly altered hornblende cemented with gypsum and anhydrite and of iron hydroxides with a minor admixture of carbonates and bitumoids.

The rocks are heavily altered everywhere; a thorough search was necessary to find inside the ferruginous crusts in some of the pipes relicts of sulfides (pyrite) also present in sandstone cement. This indicated that within ferruginated and gypsified mounts exists a zone of oxidation of sand pipes precemented by sulfides. Such pyrite-bearing pipes have been described in various parts of the Cheleken Peninsula by Dvorov [16] and mentioned by several other authors.

All these data seem to suggest a tectonic fault along which pipes of quicksand precemented by carbonate-sulfide minerals were extruded.

For hydrogen sulfide migration in water and other underground fluids the presence of carbonates is essential: as the amount of dissolved carbonates is increased, H_2S content also rises parabolically, because the two acids are in a so-called sulfide-carbonate equilibrium [54].

The mechanism of hydrogen sulfide interaction with metals is largely determined by alkalinity or salinity of the solution; the behavior of HS^- ion is important in this case.

The sharp drop of stratal pressure and the development of a solid carbonate phase in the solution saturating the sand ought to have created near the surface an alkaline medium with high pH, which in turn stimulated the activity of HS^- ions and led to the formation of iron sulfides.

The subsequent oxidation of pyrite according to the scheme of sulfuric acid weathering resulted in a transition of FeS_2 into Fe_2O_3 , raising the geochemical mobility of Fe^{3+} and helping the development of gypsum anhydrite cement widespread in sand pipes in the mounds.

Generally, eruptions in the area of Alugil mud volcano occurred not only through central vents but through cracks, and along with blocks, fragments, and mud torrents ejected from the principal vent, degassing proceeded through cracks and faults, leading to a chain of mineral neomorphs; the latter fixed rigidly the structures of sand diapirism along faults.

Traces of sand diapirism studied by us in detail in the Cheleken Peninsula do not seem to be a rare exception. Judging by the literary data [37, 45], similar structures are common near Boyadag mud volcano, in the neck of Karaburun (Western Turkmenia), in Donguzdyk upland of Kobystan (Azerbaijan), and in diapiric structures of Kyrkishluk, Nardaran-Suleiman, Kirman, and Yunusdag anticlines in the southeastern Caucasus.

Conditions favorable for the origination and development of sand diapirism have been studied by us in the eastern Ciscaucasian region and described in several previous publications [46-50]. We showed that the main motive force of this phenomenon is hydromicatization at depths of 1 to 4 km and more at high temperatures (100-180°C) and pressures (200-850 atm) inside clay deposits of sedimentary-rock elision basins (SREB).

In a system of sedimentary deposits sinking into the depth of SREB, a level of critical values of pressures and temperatures can be identified within which the transition of mixed-layer clay textures into nonswelling hydromica packets is especially intensive. The spatial position of such a critical P-T-level within an SREB is relatively stable; as sedimentary rocks subside, they pass through this level and experience mineral alterations with a continuous decompaction of clays and an increase of the stratal pressure of fluids in the zone of critical pressures and temperatures.

The plausibility of clay decompaction associated with hydromicatization of montmorillonite in various geological settings has been demonstrated in [27, 29, 30].

The thickness of the bed of decompacted clay and the stratal pressure of fluids in them seem to depend greatly on the volume of clay formations already hydromicatized and passed through the level of critical pressures and temperatures responsible for this process. The initial composition of clay sediments, their density, permeability, granulometry, and other characteristics also play an important role.

While a large volume of hydromicatized clays and their montmorillonitic initial composition and good insulating properties favor maximum decompaction, the presence of sand and carbonate collectors and draining faults has an opposite effect.

Indeed, rock collector beds (and highly permeable faults), when they sink to the level at which decompaction and high interstitial pressure zones are formed in the clays, absorb the liquefying fluid, reducing the interstitial pressure in the enclosing rocks, and gradually redistribute abnormally high stratal pressures (AHSP) laterally along a system of permeable beds or faults.

The interstitial pressure in isolated areas of sand reservoirs in the meantime may exceed the hydrostatic pressure; this in turn will cause terrigenous fragments to float upward, increase the plasticity of sands, and result in the formation of quicksand at great depths. This is how so-called horizons with inclusions and various sand or clastic dikes — manifestations of sand diapirism — are formed [49].

A set of beds of decompacted clays and quicksands is apparently present in various sedimentary-rock elision basins, characterized by the general term of AHSP. They have been found in sediments of various ages of western and eastern Ciscaucasian region, the southeastern Caucasus, Azerbaidzhan, Western Turkmenia and other oil and gas provinces.

In eastern Ciscaucasian sedimentary-rock basins, AHSP were studied by Nikolaev [34], Tkhostov [43], Anikiev [4], Durmish'yan et al. [19], and especially by Kissin [23, 24, 26].

Hydrodynamic anomalies in water-bearing and oil and gas sediments of the region are concentrated in three principal segments: in Sunzha and Tersk zones belonging to their namesake anticlinoria, and Kuma zone in the northern part of the Tersk-Kuma depression. In addition, Zhuravsk, Galyugaev, Kora, and Benoevsk districts have been identified in local structures of the basin; altogether, more than 25 instances of AHSP have been described.

High hydrostatic water heads greatly exceeding the elevation of aquifer outlets on the day surface within the Caucasus Mountains is a characteristic trait of AHSP. Thus, in the Tersk-Sunzha zone the actual hydrodynamic pressure heads rise to a level of 3000-4500 m, while calculated estimates are 300-400 m, i.e., the elevation of the outcrops of Maikop sandstones along the northern-wing of the Caucasus.

Like many oil deposits, AHSP zones are often multistratal; within a structure high pressures are observed in several adjacent aquifer complexes rather than in one.

The stratigraphic distribution of AHSP within the eastern Ciscaucasian basin described in the table compiled on the basis of Kissin's data [24, 25] are interesting.

As follows from the data, the anomalous stratal pressures were most developed in a thick clay Maikop bed; the Upper Cretaceous, composed of fissured carbonate rocks, held second place in the prevalence of these anomalies, followed by terrigenous-clay Lower Cretaceous, and, finally, terrigenous-clay Paleocene-Eocene and Upper Jurassic rocks.

TABLE 1. Stratigraphic Localization of AHSP in the Various Units of the Region

Stratigraphic subdivisions	Black mountains (Benoi, Korinsk areas)	Sunzha ridge	Tersk ridge	Galyugaev area	Kuma zone	Zhurav area
Paleocene-Eocene	—	—	—	—	—	—
Maikop	—	—	—	—	—	—
Upper Cretaceous	—	—	—	—	—	—
Lower Cretaceous	—	—	—	—	—	—
Upper Jurassic	—	—	—	—	—	—

Note: "+" = AHSP discovered by drilling; "—" = not discovered.

Above and beneath the Maikop bed, the number of AHSP sites decreases noticeably. A drop of stratal pressures from to; down should be emphasized. Thus, in Tersk-Sunzha ridges the "anomalous pressure ratio" $P_{\text{stratal}}/P_{\text{geo}}$ after Kissin [25] drops from 0.95 (Maikop) to 0.51 (Jurassic). It will be recalled that in a normal hydrodynamic environment this ratio is usually 0.457.

Some authors [4, 28, 43] have associated AHSP with the influx of liquefying fluids through faults from the depths of the earth's crust. The hypothesis of an endogenous genesis of AHSP met with objections and was incapable of accounting for the entirety of facts described in the eastern Ciscaucasian region. For example, it is unclear why most of the hydrodynamic anomalies tend to occur in Maikop clay strata, why stratal pressures in multilayer AHSP zones decrease from top to bottom, and why the composition of waters in the hypothetical fluid arrival site from the interior varies so insignificantly.

Another group of investigators [6, 32, 33] interpreted AHSP as resulting from an abrupt rise of isolated blocks of sedimentary rocks, which retained the stratal pressures of the preceding hydrodynamic levels; calculations [25] refuted this hypothesis as well.

Kissin [24, 25] seems to have approached a more plausible interpretation of the mechanism of AHSP development in this region. Proceeding from studies by Illing [62], Dickinson [60], Hubbard and Rubey [61], and other foreign geologists, he believed that the source of abnormally high pressures should be sought in the clay strata of the Maikop.

According to Kholodov's views [49], the source of fluids which created AHSP in the eastern Ciscaucasian region and probably also throughout the southeastern Caucasian region where Maikop clay sediments which passed through the stage of hydromicatization and dehydration, i.e., sank to depths of about 2000–4000 m. The fluids (water + CO₂ + H₂S + bitumoids) pressed out of the sediments at these levels accumulated and developed in the clay a zone of high pressures; when they were brought into permeable collector rocks from the clay, they easily lost carbon dioxide and cemented portions of the reservoir, thus sealing themselves inside. In some cases hydraulic ruptures occurred in sand collectors and quicksand structures were formed, which, too, resulted in a partial insulation of permeable segments. In all these situations, the dehydration of clay produced fluids under a high pressure, which in turn realized their mineral-forming or hydraulic potential in passing from one medium into another and forming AHSP zones in isolated portions of collectors.

It should be stressed that usually AHSP zones which arise spontaneously within a sedimentary cover are not long-lived formations. Linetskii [31] has estimated that with an occurrence depth of 1 km, initial pressure of 460 kgs/cm², the final (hydrostatic) pressure of 200 kgs/cm, the clay cover thickness of 100 m, and the infiltration rate of 10⁻⁹ cm/s, AHSP decreases to the hydrostatic level in about 650,000 years. In other words, against the background of geological events, these are short-lived phenomena that arise and disappear rapidly. AHSP are ephemeral in geological terms.

The traces of sand diapirism described above allow linking genetically not only the processes of hydromicatization and dehydration of clays and the development of AHSP, but the creation of mud volcanoes as well.

Mud volcanos are a typical feature of oil and gas structures in Azerbaidzhan, Southern Caspian region, and Western Turkmenia) more than 200 of these peculiar structures surrounded by fields of mud volcano material are concentrated in this territory.

Their genesis has been studied by Arkhangel'skii, Gubkin, and Shatskii; the problem has also been investigated by Fedorov, Yakubov, Gorin, Ronov, Durmish'yan, Kalinke, Zeinalov, Shnyukov, Grigor'yants, Aliev, and others [10, 13, 15, 17, 21, 39, 44, 53, 55, 58, 59].

On the basis of the ample factual data, the following regularities were established in the spatial distribution of mud volcanoes.

1) mud volcanism is confined to areas of piedmont and intermontane troughs which experience active subsidence and have a very thick sedimentary cover [13, 56, 58]; according to some authors, thick clayey strata in sedimentary rock basins are particularly favorable for the development of mud volcanoes [12];

2) the close genetic and paragenetic relationship between mud volcanoes and oil and gas deposits [14, 44, etc.]; of recent studies in this respect, special mention should be made of the work by Bunyat-Zade [7, 8, etc.];

3) a partial cooccurrence of AHSP zones of mud volcanoes; this feature was repeatedly noted by Durmish'yan [17];

4) the confinement of mud volcanoes to large anticlinal structures, sometimes very ancient; not infrequently (but not always) such anticlines have a broken-through diapiric core made of extruded clays and breccias and compounded by numerous ruptures [1, 5, 15, 44, 45]; and

5) the fact that most mud volcanoes are controlled by a net of major faults; the development of these effects is especially favored by intersection nodes of faults of two different directions [11, 57]; Putkaradze and Khalilbeili [38] and Sultanov et al. [42] believe that mud volcanoes complete the tectonic development of a structure: first a fold is formed, then a fault, and finally a mud volcano.

These regularities of the distribution of mud volcanoes seem to be best explained by a hypothesis which postulates that these units are a result of dehydration of clay beds, formation of AHSP zones, and concentration of oil and gas fluids in collector beds against the background of heightened vertical permeability and tectonic activity of a region.

The sinking of thick clay beds to a great depth and their hydromicatization and dehydration, coinciding with synsedimentary development of folds and faults, first results in a concentration of oil and gas-water fluids in clay beds and also in sand and carbonate collectors forming the anticlines. This is associated with a rise of stratal pressures because of the transformation of clay minerals, development of ancient quicksand units, and the sealing of portions of gas and oil deposits.

Subsequently, as a result of diverse geological factors, gas and water fluids periodically break out of collectors through the cracks to the day surface. The immediate causes of such eruptions could be tectonic subsidence, increased stresses as a result of folding, earthquakes, or excessive influx of fluids into the gas-water-oil system. The vertical permeability of the sedimentary cover is conducive to such ruptures.

During the course of a fluid rupture, a flow moves into cracks and brings with it clay matter and fragments of enclosing rocks; this half-liquid mass is effused to the surface, forming eruptive apparatus of volcanoes, mud volcano breccia, and mud covers [18, 21]. Besides the sedimentary matter proper, deeper elements borrowed from the thermal waters of the basement must also take part in this process [49].

Traces of sand diapirism, i.e., sand dikes and "horizons with inclusions," may apparently be formed in some cases not only at a great depth but also as a result of direct rise of quicksand to the day surface; this seems to be the case with the formation of block sandstones of the ancient Aligul volcano described earlier.

* * *

In conclusion, it should be noted that AHSP zone formation processes caused by dehydration of clay beds have been completely disregarded until now in tectonic interpretations. Yet, a catagenetic transition of montmorillonite into hydromica and the subsequent decompaction of clays create inside sedimentary strata zones of a heightened plasticity (noncompetence). Such heightened plasticity zones may be conducive to development of low-angle overthrusts [51, 52], as well as stimulate clay diapirism and the creation of diapiric and cryptodiapiric folds [10, 45]; it is even possible that entire systems of overthrust covers are to a large extent associated with internal catagenetic formations of terrigenous-clay sediments [13].

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GEOLOGIC-GEOCHEMICAL PREMISES FOR THE FORMATION OF MANGANESE ORES OF THE MANGYSHLAK OCCURRENCE

REPORT 2. ELISIONAL-EPIGENETIC MODEL OF MANGANESE ORE GENESIS*

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We compared the geologic-geochemical environment in the Mangyshlak manganese occurrence environment and a theoretical model for the formation of different manganese compounds in conditions of a normal sedimentary sequence, at low temperatures and pressures. A conclusion on the possible elisional occurrence of manganese-bearing solutions is validated. We performed a calculation on the stability of manganese compounds, which shows that only one (carbonate) form of primary manganese mineralization is possible in the examined case.

The question of the genesis of any occurrence reduces first of all to the construction of a probable model for ore formation. This is comprised of several basic elements: 1) a source for the mineral component; 2) a source for the solutions (in the case where the occurrence is hydrogenic) and the physical-chemical environment of the migration of the mineral components; 3) precipitation conditions (accumulation) of the ore mineral and the causes for the stability of the ore forming environment through time; 4) factors which prevent the epigenetic dissolution of the ore accumulation after completion of the ore forming process.

As applied to the Mangyshlak manganese occurrence, part of these elements may be set up in an alternative order: either Mn and the solutions transporting it were introduced into Oligocene-Miocene deposits from outside, at a time when ore formation was a random act; or they are borrowed from the nearest surroundings, that is from the same Maikopskian sequence, as a result of regular processes in its evolution in epigenesis.

In a geological synopsis [12] it was shown that signs of some fundamental "contamination" of Mn is noted neither above nor below the productive sequence, nor in the rocks which replace the productive packet in space. Moreover, a tendency towards a decrease in the average Mn concentration in the clays beyond the boundary is observed in proportion to the proximity of

*The article is published in a controversial series; the physical-chemical basis for the genesis of manganese ores caused serious reviewer objections — Editorial Board.

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the ore deposit, while in the same productive sequence of sand-silt material beyond the limits of the ore nodules has a regionally Clarkian background of concentration. This indicates that in the accumulation period of the Oligocene-Miocene sequence, there was no massive erosion of terrigenous material specifically enriched in Mn which could later form the occurrence.

To a degree it is evident that hydrothermal development of the productive sequence (which lies at the base of the hydrothermal-sedimentary model) could not leave a "manganese trace" on the volumes of clays adjacent to the reservoir. Even this one circumstance, apart from those cited above [12], casts doubt on the reliability of the hydrothermal-sedimentary model for the formation of the Mangyshlak occurrence.

Thus, the logical path "indirectly" leads to a search for an ore material source within the same Maikopsk sequence, modeling the probable causes for its mobilization, transport, and concentration in a localized, very small volume reservoir. In the character of the ore formation process, a similar model may be called the elisional-epigenetic model. A single principal serves as the basis of this model: as a result of the epigenetic evolution, the clays dominating the volume of the sequence "lose" an insignificant fraction of Mn, together with a portion of the pore solutions, while comparatively small volumes of sand reservoirs "accept" the ore component. As a result of the redistribution of the concentrations in a stable regime of ore deposition, an anomaly arises (the deposit), in which the degree of manganese concentration is estimated at a quantity two to three orders larger than the background. The further content of this article is devoted to features of the reliability of the elisional-epigenetic model of manganese ore genesis for the Mangyshlak occurrence.

On the basis of general theoretical premises, we note that introduction of Mn into a basin of sediment accumulation occurs by four probable means: 1) in natural compounds (manganese carbonates or oxides); 2) in the form of an admixture in rock forming silicate minerals; 3) in a sorption complex on colloidal particles of organic materials of clays or iron hydroxides; 4) in truly dissolved or complex form. Concentrated erosion of Mn in the form of natural solid compounds is random, and apparently the least typical. For this, surficial destruction of earlier formed Mn mineralizations is necessary. Moreover a similar source should appear limited in the area of the sedimentation basin, since all of the sediment types in this local region will be contaminated by Mn.

Manganese taken from the composition of the sand-silt material is presented over a more or less homogeneous regional background, the quantity of which depends on the qualities of the source rocks (age, degree of alteration, acid-alkali properties). However, the mobilization of microadmixture, including Mn, from sand-silt rocks is inhibited to a significant degree, since partial or complete destruction of the mineral containing the element-admixture is required for this, and this is possible only in the rigorous conditions of catagenesis or metamorphism.

Clays and organic colloids transport the more easily mobilized forms of elements (Na, K, Ca, Mg, Fe, Mn, etc.), since a portion of them is found in the exchange complex exclusively in ionic form (alkali and alkali-earth metals). As regards Fe and Mn, in dependence on the pH-Eh and the mineralization of the medium, the forms of their sorption may be different — from free ions of Fe^{3+} , Mn^{2+} to charged and neutral hydroxo-complexes of Fe (III), Mn (III), and Mn (IV).

Investigation of Mn migration properties in the mixing of river and sea waters in typically humid zones (Saigon and Razdol'naya rivers) showed [1] that before mineralization of the mixed waters, less than 6% the behavior of Mn in suspension is determined by sorption-desorption processes. In proportion to the growth of mineralization in the mixed waters, the labile form of Mn becomes secondary to the basic form, while associations with polar organic combinations of a primarily humic nature, which are able to bind up to 30-45% of the Mn begin to play a dominating role.

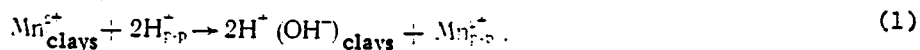
In an arid zone, where the organic component of river runoff is extremely small, oxidation-reduction conditions are created for the migration of Fe and Mn in the form of solid or colloidal hydroxides. In this case they conduct themselves more conservatively, however, they precipitate together with terrigenous material on the floor and appear in the reducing medium of the sediments. Fe and Mn at some time find migrational mobility, and participate in ionic exchange in the sorption complex of the clays.

Only the appearance in the pore solution of a supplementary concentration of anionic-ligands and cations, which compensates for the loss of Fe and Mn in the exchange complex, may

carry out inverse desorption. Acting as ligands, for Mn are aqueous solution organic compounds, and hydrocarbonate, sulfate, chlorine, and hydroxide ions; for Fe, besides those listed, are also hydrosulfide ions, which form in chloride solutions a stable complex of the type $\text{Fe}(\text{HS})_2 \cdot n\text{H}_2\text{S}$.

The pH of the medium plays an essential role in the process of clay-solution ionic exchange. Clay particles precipitated onto the floor of the marine basin are found in a solution with pH equal to 8.0-8.7, that is, one possessing alkaline properties. But already within a meter layer of carbonatized muds the pH of the pore solutions falls sharply to a magnitude of 6.8-7.1. This is connected with the aerobic fermentation of organic material and the production of carbonic acid. In noncarbonate muds which are enriched in organic material, a higher acidity of the medium (pH 6.2-6.7) may be created in proportion to the accumulation of carbonic acid, not limited by the neutralizing effect of solid carbonate.

This change in the activity of hydrogen ions from a pH ~8.5 in marine water to a pH ~6.5-6.8 in the pore solution of sediment leads to desorption of clay particles:



In this scheme, alkali, alkali-earth, and heavy metal ions emerge from the clay exchange complex displaced by hydrogen ions, whose source is the oxidation of organic material existing for a rather long time. In the case of clays from the Maikopsk sequence, which are depleted in alkali-earth metals, the yield of elements should occur in agreement with the hypothetical order, composed on the basis of earlier cited [12] chemical analyses of clays: $\text{Na} > \text{Ca}, \text{Mg} > \text{Fe} > \text{Mn} > \text{Ba} > \text{Sr} > \text{Cu} > \text{Pb}$. Ca, Fe, and Mn present the greatest interest in this order, since these elements predominate in manganese carbonate and oxide ores.

Strictly speaking, carbonate diversity in manganese ores is always presented as a solid solution of Ca, Mn, and Mg carbonates, seldom Fe, Mn, Mg. Segregation of the medium's nodular minerals (calcite, siderite, rhodochrosite) indicates that either relations between competing cations varied in the ore forming solutions, or there was variation in the acid-alkaline environment and the total amount of carbonate.

The capacity of carbonates to form complex solid solutions is a characteristic property of this mineral forming system. In every solid solution the cation position is nonequivalent, but it is particularly noted in solutions of the $(\text{Ca}, \text{Fe}, \text{Mn}, \text{Mg})\text{CO}_3$ type, since the difference in the stability constants of calcite (dolomite), on one hand, and siderite and rhodochrosite on the other, is much too great.

We will consider the mineralogical series calcite-manganocalcite-rhodochrosite, which demonstrates a trend in carbonate distribution from the flanks to the core of the Mangyshlak occurrence [12]. Equilibrium manganocalcite-calcite (Table 1, 2, reaction 1) is established when $[\text{Mn}^{2+}]_{\text{fr}}/[\text{Ca}^{2+}]_{\text{fr}} = 10^{-3.04}$.

More magnesian carbonates are formed from a decreased concentration of Ca^{2+} in the solution in relation to Mn^{2+} , and for $[\text{Mn}^{2+}]_{\text{fr}}/[\text{Ca}^{2+}]_{\text{fr}} = 10^{-2.98}$, calcite becomes balanced with rhodochrosite (Table 1, reaction 2).

However, a sharp boundary of $\text{CaCO}_3:\text{CaMn}(\text{CO}_3)_2$ does not exist in nature in the same way as the boundary of $\text{CaMn}(\text{CO}_3)_2:\text{MnCO}_3$. Theoretical calculation of the continuous series $\text{Ca}_{0.99}\text{Mn}_{0.01}\text{CO}_3-\text{Ca}_{0.98}\text{Mn}_{0.02}\text{CO}_3-\text{Ca}_{0.97}\text{Mn}_{0.03}\text{CO}_3$ showed that the value of Mn/Ca in solution and in complex carbonate is best described by the expression

$$\frac{\text{Mn}}{\text{Ca}}(\text{carbonate}) = 6.5 \lg \left(\frac{[\text{Mn}^{2+}]_{\text{fr}}}{[\text{Ca}^{2+}]_{\text{fr}}} (p-p) \div 3.04 \right).$$

From this expression it follows that for formation of comparatively "pure" calcite with a formula of $\text{Ca}_{0.99}\text{Mn}_{0.01}\text{CO}_3$, it is necessary that in the mineral forming solution the ratio of the activities of free ions $[\text{Mn}^{2+}]_{\text{fr}}/[\text{Ca}^{2+}]_{\text{fr}}$ should equal $10^{-3.90}$, that is, the activity of the calcite should exceed the activity of manganese by 3.5 orders.

"Pure" rhodochrosite ($\text{Ca}_{0.97}\text{Mn}_{0.03}\text{CO}_3$) is formed in a solution where $[\text{Mn}^{2+}]_{\text{fr}}/[\text{Ca}^{2+}]_{\text{fr}} \geq 10^{-2.98}$.

Mineral stability in the calcite-rhodochrosite series depends not only on the large or small presence of Ca^{2+} in the solution. Significant competition for "control" of the carbonate ion is indicated by Fe^{2+} ; the stability of its carbonate, by the estimates of some investigators, is close to the stability of MnCO_3 [9], while in data presented in [3], natural rho-

TABLE 1. Values of Gibbs Free Energy Utilized in the Calculation (p = 1 atm, t = 25°C)

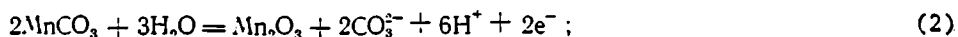
Compound	G, kcal/mole	Source	Compound	G, kcal/mole	Source
CaCO ₃ calcite	-269.58	[9]	MnO ₂ pyrolusite	-111.19	[9]
MnCO ₃ natural rhodochrosite	-195.7	[3]	Mn ₂ O ₃ kurnakite	-210.3	[9]
CaMn(CO ₃) ₂ natural kutnahorite	-400.2	[3]	MnCO ₃ birnessite	-108.3	[3]
FeCO ₃ siderite	-102.6	[9]	FeS pyrite	-38.9	[9]
			Fe(OH) ₃ (free in the sediment)	-107.8	Calculation

TABLE 2. Carbonate Forming Reactions and Their Constants

Reaction No.	Reaction	Reaction constant (t = 25°C, p=1 atm)
1	CaMn(CO ₃) ₂ - Ca ²⁺ = 2CaCO ₃ - Mn ²⁺ kutnahorite calcite	[Mn ²⁺] _{fr} [Ca ²⁺] _{fr} = 10 ^{-10.04}
2	MnCO ₃ - Ca ²⁺ = CaCO ₃ - Mn ²⁺ rhodochrosite calcite	[Mn ²⁺] _{fr} [Ca ²⁺] _{fr} = 10 ^{-2.56}
3	FeCO ₃ + Ca ²⁺ = CaCO ₃ - Fe ²⁺ siderite rhodochrosite	[Fe ²⁺] _{fr} [Ca ²⁺] _{fr} = 10 ^{-2.00}
4	MnCO ₃ - Fe ²⁺ = FeCO ₃ - Mn ²⁺ rhodochrosite siderite	[Mn ²⁺] _{fr} [Fe ²⁺] _{fr} = 10 ^{-0.55}

dochrosite is more stable than siderite (see Table 1, reaction 4). For rhodochrosite and kutnahorite we utilized thermodynamic data [3] obtained for natural minerals, which made it possible to reanalyze intertransitions in the series calcite-manganocalcite-rhodochrosite.

The state of the oxidation-reduction environment significantly influences the stability of manganese carbonates:



$$\text{Eh} = 2,10 - 0,177\text{pH} + 0,029 \lg [\text{CO}_3^{2-}]^2;$$



$$\text{Eh} = 2,128 - 0,177\text{pH} + 0,029 \lg [\text{CO}_3^{2-}]^2.$$

Reaction equations (2) and (3) demonstrate the oxidation-reduction levels of the transition of divalent into trivalent manganese.

However, at the same time, a series of complex combinations of Mn(II), Mn(III), and Mn(IV) with oxygen is formed in the reaction products.

On the whole, for the characteristics of Mn mobilization conditions and its association in carbonates and oxides it is necessary to examine a multiple component system with participation by Ca and Fe: the competitors with Mn in carbonate and oxide compounds. The inclusion of Mg in the system is apparently inadvisable due to the low stability of pure magnesium carbonate.

The stability fields of different Mn and Fe compounds are presented on diagrams (Fig. 1) in pH-Eh parameters for the condition of equilibrium of the carbonate system in CaCO₃ at t = 25°C and p = 1 atm. The calculation was performed for the following cases: for sulfides: pyrite and alabandite at the sum of concentration of the S²⁻ compounds equal to 10⁻² moles; for carbonates: manganocalcite, rhodochrosite, and siderite, with agreement of their stability constants and reactions (2) and (3), for the sum of the carbonate components equal to 10⁻² moles; and for oxide compounds, assuming an active concentration of [Fe²⁺] and [Mn²⁺] equal to 10⁻⁵ moles.

Diagrams of similar outer appearance have been represented at one time E by Goshe [3], but for extremely high concentrations of $\sum(\text{carb}) = 10^{-1.4}$ moles and $\sum\text{S}^{2-} = 10^{-1}$ moles, while by M. F. Stashchuk [13] in trivariant Eh-pH-pCO₂, where the activity of [Fe²⁺] and [Mn²⁺] are also unreally overestimated (10⁻³ moles) in application to the natural environment.

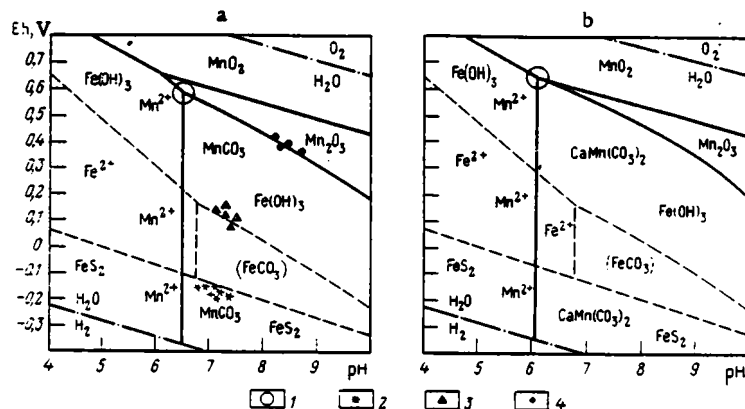


Fig. 1. Diagrams of the stability of compounds containing Fe and Mn. a) Rhodochrosite, b) manganocalcite. 1) Region of oxidation of manganese carbonates into oxides; 2) region of modern pore solutions from sand-silt sediments of the Turkmen'sk gulf with the intense appearance of sulfate-reduction; 3) pore solutions from shelf sands of sediments from the Caspian (Cheleken peninsula); 4) Caspian sea water. Solid lines show the stability boundaries for Mn containing compounds, dashed lines show Fe containing compounds (thermodynamic data are dependent on [1]).

On our diagrams (see Fig. 1), solved mainly relative to Mn compounds, parameters $\sum \text{carb}$, $\sum \text{S}^{2-}$, $[\text{Mn}^{2+}]$, $[\text{Fe}^{2+}]$, are selected. Their magnitudes are characteristic for young sediments from the shelf portions of interior basins. The stability fields of Fe compounds are located conditionally to a large extent, mostly in order to stress the potential defining role of Fe-oxide and sulfide barriers [2, 5, 13].

In analyzing the diagrams, we at once note a major feature in the behavior of mobile forms of Fe and Mn: the area of the stability field of Mn^{2+} (MnCl^{2+} , MnCl^+ , MnCl_2° , MnSO_4° , MnHCO_3^+ , MnOH^+) far exceeds the area of the stability field of Fe^{2+} (FeCl_2^+ , FeCl_2° , FeSO_4° , FeHSO_4^+ , FeOH^+). From above, in Eh-pH parameters, the Fe^{2+} field is limited by an oxidation barrier of $\text{Fe}^{2+}/\text{Fe(OH)}_3$ (dotted line). Below, the stability of divalent iron is controlled by the presence of sulfur sulfide. For simplification of the structure of the " Fe^{2+} -sulfide" boundary, the relatively most stable form of iron sulfide, pyrite, is used, although it is known that the action of hydrogen sulfide on Fe compounds forms a complete series of sulfide minerals with different stoichiometries of Fe(II) and Fe(III) [13].

In distinction from Fe, manganese sulfide is unstable, if it proceeds from the activity assumed in the calculation of $[\text{Mn}^{2+}]$ and the sum of sulfur sulfide. The alabandite field is completely displaced by rhodochrosite or manganocalcite. The appearance of a stable form of Mn is possible only in exceptional conditions ($\text{pH} > 8.5$; $\sum \text{S}^{2-} > 10^{-4.5}$ mole).

If equality of $[\text{Fe}^{2+}]$ and $[\text{Mn}^{2+}]$ concentrations existed in natural conditions, as we conditionally assumed for the calculation of the diagram, then formation of siderite and rhodochrosite would have been approximately equally probable, but manganocalcite had an advantage over siderite due to the generally increased active concentration of calcium in comparison with $[\text{Fe}^{2+}]$ and $[\text{Mn}^{2+}]$.

However, in actual natural conditions the Clarke of Fe is two to three orders higher both in rocks and in water. In connection with this, specific conditions are necessary for the formation of manganese carbonate, where the migration of divalent iron is inhibited. Two such levels exist, in agreement with the diagram (see Fig. 1a). First, this is a medium which corresponds to the carrier $\text{Fe}^{2+}/\text{Fe(OH)}_3$, where the mobility of iron is controlled by the solubility of its hydroxides. The group of points represented on this boundary reproduce the oxidation-reduction environment in modern sand sediments of the Caspian on the open coasts of capes which protrude far out into the sea (Cheleken peninsula). Here, in pore solutions of sediments at depths of 1-3 m from the surface of the floor, the active concentration of Fe on the average is equal to $10^{-5.2}$ moles, which corresponds to Eh-pH coordinates to a mobile equilibrium

of $\text{Fe}(\text{OH})_2$ - FeCO_3 , while nonetheless, no authigenic siderite is formed, due to the small amount of carbonate in the solutions $\sum_{(\text{carb})} 10^{-3}$ moles [5].

In these conditions formation of MnCO_3 is also impossible (the competition with the FeO aspect), moreover the Mn content in the pore solutions is an order smaller than the Fe content. Consequently, regardless of the fact that the position of the points in Eh-pH coordinates formally corresponds to the MnCO_3 stability field, the medium of aerated sand sediments which contains an insignificant quantity of organic material does not assist in the accumulation of manganese carbonate, on one hand due to the small overall amount of carbonate, and on the other hand due to the deficit of Mn^{2+} in comparison with Fe^{2+} .

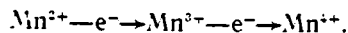
A different situation is observed in an environment of high reduction of the medium, which is controlled by the sulfide-sulfate (H_2S - S^{0} - SO_4^{2-}) barrier. Only in this environment may the concentrations of $[\text{Fe}^{2+}]$ and $[\text{Mn}^{2+}]$ be compared, while for high values of $\sum \text{S}^{2-}$ the content of mobile Mn further exceeds those for Fe, the concentrations of which are determined by the solubility of its sulfides in mineralized solutions. The group of points lying close to the "sulfide-sulfate" boundary meets the conditions of organic containing sand sediments deposited in shallow water bays of the Caspian sea eastward from the Cheleken peninsula, in which Mn contents reach 0.1-0.5%. This medium also corresponds to the Mn^{2+} - MnCO_3 equilibrium, but, as in the Fe oxide barrier, authigenic manganese carbonate is not recorded here either, although the total Mn content in these sediments is 1.2-2 times higher than the regional Clarke value. This is connected not with the Fe competition aspect, but with the significant reserve of Ca (carbonate fauna) in coastal sand sediments.

As already noted, calcite is a more stable phase in relation to rhodochrosite, if the active concentration of $[\text{Ca}^{2+}]$ exceeds the concentration of $[\text{Mn}^{2+}]$ by more than 2.5 orders (this corresponds to analyses of pore solutions). Thus, for formation of MnCO_3 , in addition to a source of Mn^{2+} inflow, a hydrogen sulfide-carbonic acid solution with minimal Ca and Fe content is necessary.

In a hydrogen sulfide-carbonic acid medium, in sediment with a low Ca content and a close to neutral pH, the migration of Fe^{2+} is inhibited by sulfide, $\text{Fe}(\text{OH})_2$ is predominant in hydrotroilite (melnikovite), and ionic or complexing Mn may be accumulated in the solution up to equilibrium with the third phase of MnCO_3 . This environment is generally characterized by a total amount of carbonate greater than 10^{-2} moles, which assists in the formation of rhodochrosite, manganocalcite, and calcite. The relations between these minerals are established in conformity with the Ca^{2+} contents in the pore solution. The presence of small quantities of Ca^{2+} leads to the predominance of rhodochrosite and manganocalcite. For higher Ca concentrations, the Mn portion in complex carbonates becomes negligibly small, and all of the carbonate is consumed in the formation of practically "pure" calcite.

Thus, from analysis of the diagram (see Fig. 1) it follows that in hydrogen sulfide pore solutions (pH 6.5-7.5; Eh 120-200 mV) for the presence of sufficient quantities of Mn^{2+} , the most characteristic association of minerals is: pyrite-rhodochrosite-manganocalcite-calcite; in a nonhydrogen sulfide reducing environment (pH 6.5-7.5; Eh + 100- -100 mV) the association is: siderite-rhodochrosite-manganocalcite-calcite; in a weakly oxidizing environment (pH 6.5-7.5; Eh + 200- +100 mV) the association is: rhodochrosite-manganocalcite-calcite-limonite.

There are several remarks relative to mineral forms of manganese with higher valence. If the solution does not contain carbonates and is found under the influence of free oxygen, then divalent manganese is oxidized, forming compounds similar to Fe oxides. For very high oxygen potential the most stable form of four-valent manganese is MnO_2 (pyrolusite). However, actual media, first, do not occur absolutely without carbonate, and second, oxidation-reduction reactions always have both oxidized and reduced forms in their end products, which to significant degree "entangles" the theoretical sequence:



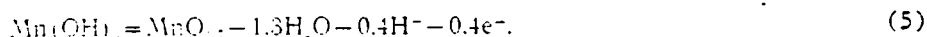
The trivalent manganese oxide field (see Fig. 1) is always overlapped to some degree by the carbonate field, therefore by oxidation of Mn^{2+} to Mn^{4+} , manganite Mn_2O_3 becomes its type of metastable phase. Apparently, this may explain the fact that in the presence of rhodochrosite, pyrolusite MnO_2 is not the basic oxide phase, while a series of minerals exists with different content of manganese valent forms, from birnessite to todorokite and cryptomelane. A continuous series of divalent manganese oxides may be expressed by the theoretical sequence:

Mn^{2+} -birnessite-todorokite-cryptomelane-pyrolusite, or by abstract and far from accurate molecular formulas: Mn^{2+} - $\text{MnO}_{1.5}$ - $\text{MnO}_{1.7}$ - $\text{MnO}_{1.9}$ - MnO_2 .

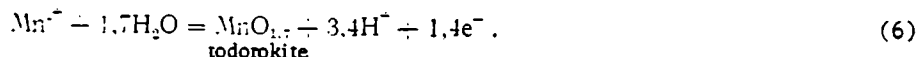
In the initial stage of Mn oxidation, a phase of the trivalent state inevitably occurs by the scheme:



but if the source of Mn^{2+} is constant, and a high oxidation potential is also constant, then hydroxide of trivalent manganese may not exist in the form of an independent compound and it decomposes into conventional todorokite, in agreement with the Eh-pH transition of $\text{Mn}^{2+} \rightleftharpoons \text{Mn}_2\text{O}_3$,



Then reaction(4) and (5) combined give



Performing calculation of the reaction in Eh-pH parameters (Eh = 1.315-0.143, pH=0.042 lg $[\text{Mn}^{2+}]$), it is not difficult to be convinced that the graph of this function on the diagram exactly corresponds to the line of the $\text{Mn}^{2+} \rightleftharpoons \text{Mn}_2\text{O}_3$ transition.

A form of pyrolusite is not formed with further oxidation of todorokite in the presence of Mn^{2+} . Cryptomelane occurs here as the oxidized compound, while a mineral with the molecular formula of birnessite occurs as the reduced form:



It is evident that only cryptomelane ($\text{Na, K, Mn} \cdot 15\text{MnO}_2 \cdot n\text{H}_2\text{O}$ or a similar compound, saturated by four-valent manganese, is enabled by oxidation and dehydration to form pyrolusite with a simultaneous output of partially reduced Mn, of the component mineral type nsutite or birnessite:



Finally, if by some cause the source of Mn^{2+} input is disrupted, all of the manganese minerals from the $\text{MnO}_{1.5}$ - MnO_2 transition group are transformed into a phase that is more stable in highly oxidizing conditions, that is, pyrolusite.

Analysis of the forms of oxidation of rhodochrosite (see Fig. 1a) and manganocalcite (see Fig. 1b) has an extremely interesting consequence. The Eh-pH fields are designated by small circles on the diagrams. Oxidation of Mn^{2+} occurs here, in equilibrium with solid phase as a result of acid solution of the corresponding minerals. If a transition into oxides of trivalent manganese (manganite) is a characteristic of pure rhodochrosite, then manganocalcite in equilibrium with calcite is oxidized directly up to a higher valence form of manganese, forming a compound saturated in MnO_2 (cryptomelane, pyrolusite).

This theoretically recognized rule finds reflection in actual material. It is known that in Mangyshlak, where pure rhodochrosite is rare, the most characteristic mineral oxides are birnessite, todorokite, cryptomelane, and pyrolusite, but there is no oxide of Mn(III), that is, manganite. Conversely, in the Nikopol'sk occurrence, rhodochrosite dominates the composition of carbonate ores, and consequently a layer is traced in the oxidation zone that is saturated by oolite-resembling manganite disseminations which completely correspond to the physico-chemical processes of oxidation of MnCO_3 through Mn_2O_3 into MnO_2 .

An indirectly conducted test is confirmed by calculations on the effects of complex manganese oxides with water [15]. A solid solution of oxides $(\text{MnO}_2)_{2n-3} \cdot (\text{MnOOH})_{4-2n}$ (where n varies from 1.5 to 2.0) responds sensitively to the pH of the water solution in equilibrium with it. In an alkali region (pH 8.5), the complex oxide is represented mainly by MnOOH , but the portion of MnO_2 grows rapidly in proportion to the acidification of the medium, reaching almost 100% for a pH below 6.0.

On the whole, analysis of the geochemistry of Mn-containing compounds on a background of competing Ca and Fe effects make it possible to draw some preliminary conclusions: 1) if mobilization of Mn^{2+} from terrigenous material depends on the acidity of the medium (and acidity

at the level of diagenesis and early catagenesis of sediments is set by the acid gases CO_2 and H_2S , generated in the processes of biogenic sulfate-reduction), then the intensity of Mn outtake into the solution indirectly depends on optimal conditions for sulfate-reduction (inflow of SO_4^{2-} , organic material) and directly on the Ca and Fe content in the liquid and solid phases, which influences the concentration of the acid components through carbonate and sulfide formation; 2) the migrational properties of Mn^{2+} depend on the state of the oxidation-reduction environment and amount of carbonate in the solution; 3) fixation of Mn^{2+} in the form of carbonates is found in dependence on the concentration of competing cations (Fe^{2+} , Ca^{2+}). Manganese carbonates are not formed with their surplus; 4) oxidation of manganese carbonates occurs under the influence of high oxygen potential, while the level of Ca concentration, and more precisely the pH of the medium, determine valence forms of Mn oxides.

Becoming familiar with the calculated data on the stability of different manganese compounds, we attempt to reproduce the accumulation environment of ore mineralization from the Mangyshlak occurrence. A productive sand-silt sequence of the lower part of the Middle Oligocene was deposited during a period of formation of dry land in the region of Karatausk maganticline. In essence, these were especially shelf deposits, related by I. P. Druzhinin [8] to the facies groups of silt sediments of the wave zone and to silt sediments of marine current zones. At a distance from the Karatausk structure, sand-silt sediments alternate rapidly with silty clays of an extremely characteristic material composition. They are practically without carbonate, with traces enriched by organic material of humic and sapropelic origin.

As was shown by V. N. Kholodovii [16], a humid warm climate predominated in the source regions of the Oligocene basin (Russian platform, Urals, Caucasus islands), causing wide dispersal of wooded landscapes. In his opinion, carbonate material was inferior to sand-clay and clay in the source of the Oligocene basin (in distinction from Cretaceous) in connection with the deepening of erosion and the introduction of Devonian, Silurian, Cambrian and Precambrian Russian platform deposits into the erosional cycle. River runoff certainly abounded in humic material, which makes it possible to assume an acid weakly reducing environment of the medium. This assisted in the mobilization of a complete series of elements from the rocks of water-collectors, including are forming elements. In particular, the outtake of Fe and Mn may be accomplished both in the composition of metal-organic complexes, and in a sorbate state on the surface of organic and clay colloids.

It is possible to propose that warming and humidization of the climate in early tertiary time were stimulated by a relative increase of the partial addition of CO_2 in atmosphere. The "Parnikov effect" and a surplus of carbonic acid assisted to a similar degree in the revitalization of plant bioproductivity both on dry land and in the photic zone of the marine basin. If this is so, then the hydrochemical runoff of calcium was already "intercepted" in the peripheral portions of the basin on the boundary with a large source region (the Russian platform), while suspended flows, depleted in Ca but enriched in organic materials, reached the inner portions of the seas.

The absence of carbonate detritus in a large part of the Maikopsk clay sediments may be explained by the abundance of organic material carried away, on the basis of the following assumptions. If much organic material was carried away, while the Maikopsk basin had normal salinity, then at small depths the gas medium already did not correspond to equilibrium with the atmosphere (N_2 , O_2), and it was characterized by hydrogen sulfide contamination due to sulfate-reducing processes occurring both at the sediment surface and in the sequence of near floor marine water.

This type of basin is distinguished by sharp biological stratification. The upper aerated water layer and the lower water may abound in different plant and animal forms of life, but the existence of organisms with oxygen respiration is impossible below the "oxygen-hydrogen sulfide" boundary.

It is very probable that hydrogen sulfide depressions of the Maikopsk sea were peculiar traps for many living organisms. The large content of relicts of both humic and sapropelic material in the clays may serve as convincing evidence for this. The absence of the remains of large mollusks again confirms the notion that hydrogen sulfide contamination of the floor and constant variation of the "hydrogen sulfide barrier" displaced them to the most coastal, aerated portion of basin.

D. G. Sapozhnikov assumed that there was hydrogen sulfide contamination of the Maikopsk basin, as well as that its waters "could contain huge masses of manganese" [11, p. 19], apparently on the basis of information on increased Mn contents in the hydrogen sulfide zone of the Black sea (up to 0.5 mg/liter) and in some basins of the Baltic (0.37 mg/liter) [14].

This is easily explained from positions cited above. Acid products of sulfate-reduction reactions (CO_2 and H_2S) assist in the desorption of clay and organic particles, as well as in the reduction of Fe and Mn oxide films which are located on suspended matter. The first separation of Fe and Mn already occurs here, in the basin's hydrogen sulfide contamination zone. Iron is fixed in form of sulfides, while manganese is located in hydrous solution states associated with organic and inorganic ligands. Sulfate reduction reactions continue to flow in the later stage of mud diagenesis, but they have already slowed (the "glowing" regime), from which the concentration $\sum$ (carb) necessary for the sedimentation of Mn carbonate may not always increase in the pore solution.

The "glowing" regime of sulfate-reduction in muds is explained by the gradual processing of reacting organic material, as well as by the slow diffusion flow of sulfate-ion into the reaction zone.

Conversely, sulfate reduction proceeds more swiftly in sand-silt sediments on account of the mobility of the water solutions, with a larger output of the acid gases which are the final products, in comparison with muds.

On the modern Caspian shelf, close to the surf zone under the conditions of a mildly sloping shore dissected by bays, a specific type of sediments forms: sand-algae, in which clusters of algae and grasses with remnants of plankton are mosaically included in the sand. A characteristic of these formations is that Mn contents are extremely high (up to 0.5%), while in the pore solutions, the concentrations of $\sum$ (carb) reach magnitudes of $4 \cdot 10^{-2}$ moles, while $\sum \text{S}^2$ reach $2 \cdot 10^{-2}$ moles [6].

The flow of sulfate-reduction reactions is also retarded in the sand-silt sediments after their overlap by mud layers; hydrochemical inhomogeneities in the "sand-clay" system are gradually leveled off through diffusional exchange. For a while this complex is as if preserved until the moment when opening of the reservoir and movement of the pore solution through it occur.

Since ore formations of the Mangyshlak occurrence (carbonate concretions and caryolite oxides) are localized in the permeable sand-silt sequence and are absent in clay, then it is safe to assert that mineralization was created by gravitationally mobile hydrous solutions. Judging by the form of the carbonate nodules, movement of the solutions was extremely slow, meeting the conditions of the stagnant regime. In an active hydrodynamic regime it is probable that the formations would not be rounded, but layered, elongate, and complexly dendritic, such as caryolite oxides appear that formed in the more mobile solutions of the oxygen zone.

Introduction of manganese bearing solutions into the sand horizons is completely natural, since the sand horizons, breached by faults, were the sole drains of elisional waters from the clay sequences. This introduces the question: why was the manganese mineralization not deposited in the clays which served as the solution source? The basic feature of the clays of the environment surrounding the occurrence is that they are practically without carbonate. Portions of biogenic carbon, formed into carbonic acid in the process of destruction of organic material, was apparently insufficient for the formation of MnCO_3 , and fixing it in clays.

Activation of the hydrodynamic regime in the Maikopsk sequence arose with the revival of fracturing in which coupling of the Kapatausk meganticline with the Chakyransk syncline occurred. Increase of vertical and stress tensions in the clay sequence caused squeezing of the mud solutions, first in the sand sequence, and subsequently by fracture to the surface. Increase in the movement rate of elisional solutions in the reservoir immediately raised the level of sulfate-reduction reactions not only in connection with the dynamics of their waters, but also due to the entrance of new portions of organic materials and sulfate containing waters from the clay packets.

These solutions, being hydrogen sulfide, carried a relatively small quantity of Fe (in the form of hydrosulfide complexes), not comparable with Mn in concentration, distinguished from the exchange complex of clays and accumulated in the mud solution.

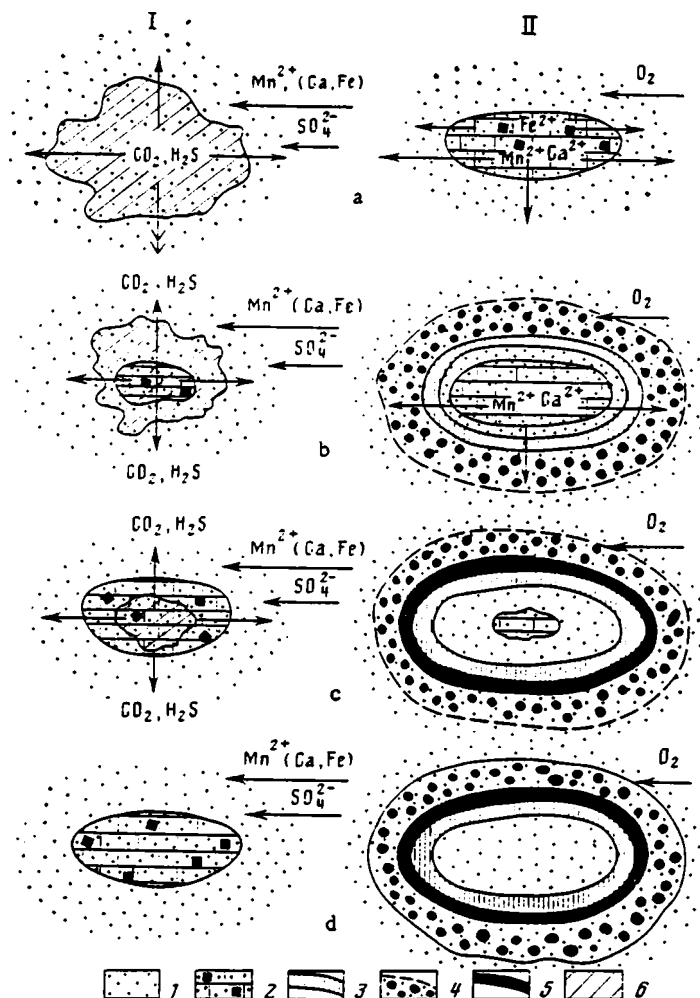


Fig. 2. Principal scheme for the formation of manganese nodules and caryolites: I) carbonate (initial); II) oxide (initial). 1) sand-silt rock; 2) manganese carbonate and calcite with mixture of iron sulfide; 3) iron concentric zone; 4) cementation zone of friable manganese oxides (birnessite); 5) dense todorokite-cryptomelane concentric zone - final stage of oxidation; 6) clusters of organic material.

The active generation of sulfate-reducing carbonic acid and hydrogen sulfide was renewed on organic "nodules" in the sands (remnant or formed in the process of out-take from the clays), and they gradually, in proportion to the "wearing" of the organic material, began to replace mineral associations: calcite, manganocalcite, and rhodochrosite with small mixture of iron sulfide (Fig. 2, I).

Apart from an Fe deficit, the practically noncalcium bearing nature of the ore-forming solutions plays an important role in the successful formation of a carbonate-manganese occurrence. As was already discussed above, if the Ca concentration in the solution exceeds the Mn concentration by three orders, then the nodules in sand-silt rock would have been cemented by calcite. Similar calcite nodules are observed in some sand horizons of the red sequence of the Pliocene, in upper Pliocene and Quaternary deposits of Western Turkmeniya (Cheleken, Boya-Dag, and Monzhukly structures). Tumorous calcitization is widely present in the Apsheronsk clays which border an active draining fault on the Chelekensk structure.

The constant presence of a sharply reducing medium in the Maikopsk clays, extending from their time of deposition to the present, predetermined their different migration of Mn and Fe. Carrying out of the Fe was retarded by sulfide deposition in clays; if this did not occur, then siderite appeared in the place of manganese concentrations. The clay sequence apparently

served as the longtime source for the introduction of Mn into the reservoir horizons. Having a significant mixture of silt material, under the conditions of an elisional regime, this sequence could have been relatively permeable to native pore solutions both vertically and laterally. In addition, it is impossible to underestimate the additional possibility of diffusional Mn movement from adjacent clay volumes to the center of crystallization of Mn carbonate in the reservoirs, which were simultaneously active centers of sulfate-reduction reactions. At the same time, it is not necessary to consider that all the carbonate of the ore nodules exists as product of biogenic reworking of organic material included in sand-silt horizons.

Elisional solutions supplied hydrous solution organic material, and also Mn and hydrocarbonate, possibly even in a saturated state compared to MnCO_3 . However, the conditions of supersaturation (also meaning mineral formation) only arose in the reservoirs at the centers of biogenic generation of H_2S and CO_2 , which predetermined ore formation in the sands, not in the clays which supplied the source components.

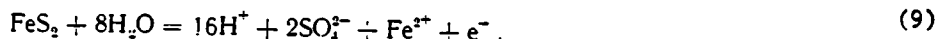
As is already understood, a contrasting lateral mineralogical zonality of carbonates has not developed at the Mangyshlak occurrence, if one does not consider the relative increase in the Mn fraction in manganocalcite in the direction towards the ancient focus of the discharging fault within the limits of the Karatausk meganticline. Extremely conditionally, this tendency may have represented the series $\text{CaCO}_3 \rightarrow \text{CaMn}(\text{CO}_3)_2 \rightarrow \text{Mn}(\text{CO}_3)$, which indicates the gradual purification of remnant Ca from the ore forming solutions.

As regards the local development of siderites in the clay sediments of the Uzunbassk suite, they already demonstrate another process, possibly unconnected in time with basic manganese ore development. There may be a possibility that the Uzunbassk siderites are a product of the diagenetic redistribution of material from initially high iron muds, not themselves subjected to deep hydrogen sulfide contamination because of better oxygen "ventilation" in the sediment accumulation basin, or owing to its significant distillation.

On the basis of the "average" composition of mud waters which occur in the stage of sulfate-reduction reworking: $\text{Cl}^- > \text{HCO}_3^-$; $\text{Na}^+ > \text{Mg}^{2+} >> \text{Ca}^{2+}$; and on the characteristics for inland seas, it would have been more warranted to anticipate mineralogical zonality of the following form in the manganese ore process (in the course of an ore forming solution): $\text{CaMg}(\text{CO}_3)_2 - \text{CaCO}_3 - \text{FeCO}_3 - \text{CaMn}(\text{CO}_3)_2 - \text{MnCO}_3$.

However, a similar zonality does exist in the Mangyshlak occurrence, possibly because of solid sulfide fixation of Fe in clays and impoverishment of the clays in alkaline earth metals.

We will dwell in more detail on the mechanism of oxidation of manganese-carbonate concretions after erosional uncovering of the occurrence and the action of oxygeneous waters. It may be seen from Fig. 1 that the stability field of MnCO_3 and $\text{CaMn}(\text{CO}_3)_2$ in Eh-pH coordinates is quite large, and this shows that its oxidation should precede initiating processes, assisting in the withdrawal of Mn into solution. Apparently, micromixtures of Fe sulfide begin to oxidize first. Their presence is established on ocherous inclusions in carbonate concretions.



Local increase in the acidity of the concretions, interiors causes etching of carbonates, which on the one hand increases the permeability of the body of the concretion to solutions, while on the other hand it leads to the mobile state of Fe^{2+} , Mn^{2+} , and Ca^{2+} :



Divalent Fe diffusionally migrates beyond the limits of the sulfide oxidation zone, which on the whole coincides with the concretion's surface. Here, in connection with reaction (10), the acidity of the medium falls sharply, and Fe^{2+} oxidizes to $\text{Fe}(\text{OH})_3$, forming the first iron concenter (see Fig. 2, II). Oxidation of Mn^{2+} becomes possible only when even an insignificant mixture of the sulfide which plays a stabilizing role for Mn^{2+} does not remain in the body of the concretion, since due to reaction (9), an oxygen deficit is preserved near the iron concenter for a long time. The buffering properties of the oxidation-reduction pair $\text{Fe}^{2+}/\text{Fe}^{3+}$ prevent the formation of manganese oxide with a high MnO_2 content in the initial moment of Mn^{2+} oxidation. In these conditions, the most important is the formation of friable cementation of sand by Mn oxides (beyond the limits of the iron concenter), where the birnessite ($\text{MnO}_{1.5}$) forms predominate.

As soon as the $\text{Fe}^{2+}/\text{Fe}^{3+}$ pair is rearranged to be potential defining, and for the condition of constant oxygen upflow, the Eh-potential increases sharply. In agreement with reactions (6)-(8), the multiple stepped oxidation of divalent manganese begins; during this the acidity of the medium inside the forming caryolite gradually increases, assisting in the increase of the MnO_2 fraction in complex oxides. The todorokite-cryptomelane concentrer lies close to the series of oxides, forming a low permeability cementation layer (see Fig. 2, II). In this period the permeation of oxygen inside the caryolite and the opposed carrying out of Mn^{2+} from the core to the periphery is hindered due to the sealing off of pore space by the dense Mn oxides. However, the oxide "jacket" will not be homogeneous in thickness and permeability. It is probable therefore, that exposed rounded forms of carbonate concretions are altered with oxidation to the angular, complexly dendritic caryolites with clearly expressed protuberances which are characteristic of the mineral forming process in an anisotropic medium.

There is no doubt that stabilization of the oxidizing-reducing environment in Fe and Mn oxide reactions is much obligated to the activity of microorganisms, and when applied to Mn, the oxide of which requires a very high value of Eh-potential, this process would be of low probability without biocatalysis.

Thus, by examining the reason for the formation of the Mangyshlak manganese mineralization, we may distinguish several necessary geologic-structural and geochemical conditions.

The geologic-structural environment of the mineralization is characteristic of the presence of an elisional paleobasin and the corresponding hydrodynamic regime of sedimentogenic waters, which under influence of vertical and tangential stresses are set free from the clays and flow into incompressible reservoirs, and from there along tectonically weakened zones to the surface. In an elisional hydrodynamic regime every permeable fault plays the role of a drain for sedimentogenic waters, and the more permeable it is, the more rapidly and completely the pore solutions are squeezed out from the clays. Apparently, a system of fracture dislocations was a similar drain for ore forming solutions in the connection zone of the Karatausk meganticline with the Chakyransk syncline.

The geochemical side of the question includes the following necessary premises: 1) the specifics of the regions which serve as the paleobasin sources, first of all in the relation of noncarbonate terrigenous clay material and the abundance of humic runoff; 2) the specifics of basin sedimentation, which probably includes the hydrogen sulfide contamination of the sequence's waters; 3) the specifics of clay sediment diagenesis, which occurs in a medium where calcium carbonate is practically absent. This all leads to the situation when natural separation of the Fe and Mn migrational paths occurs in the pore solutions from the sequence of Maikopsk clays for the constant presence of sulfate reducing hydrogen sulfide and carbonic acid. Calcium and iron, which are constant competitors of Mn in carbonate formation, do not reach saturation in carbonate due to their different natures. Only under these conditions may rhodochrosite and manganocalcite precipitate in solid phase, again for sufficiently high partial pressure of carbonic acid which is achieved in the reservoir's voids on centers of sulfate-reducing gas generation.

Analysis of the properties of elisional paleobasins make it possible to confirm that not only carbonate-manganese and siderite occurrences [16] may be formed on their periphery in the different geochemical environments, particularly in tectonically weakened zones, but that deposits of elementary sulfur [7], and low temperature polymetal ores [10] may also be formed.

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NEW DATA ON THE PALEO GEOGRAPHIC CONDITIONS OF FORMATION OF TIRASSK ROCKS
OF THE CARPATHIANS IN CONNECTION WITH THEIR SULFUR CONTENT

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UDC 551.88(477.4)

Results of studies on the lithofacies of productive Tirassk rocks in one of the areas of the southeast Carpathian sulfur-bearing basin are presented. On the basis of these findings, the paleogeography at time of deposition in this area is reconstructed. The stages of development and widespread distribution of paleoseb-kha facies are shown. It is established that the localization of metasomatic processes forming native sulfur and consequently of the deposits was caused by the lithofacies of the productive beds, which in turn were related to the paleogeographic situation.

Studies of the upper Tortonian gypsum-anhydrite deposits of the Soviet Carpathians have been pursued for almost a century and a half. Over this time period, a number of different environments of deposition have been proposed. Study intensified after 1950, when sulfur workings in the Carpathians, based on these sulfate rocks, were opened. Most investigators currently refer these sulfate formations, which are widely distributed around the Carpathians, to sedimentation in a Tortonian evaporite basin [1, 4, 7, et al.]. According to Khrushchov [15], an immense Tortonian evaporite deposit occupies an area of 81,000 km² and occurs in the

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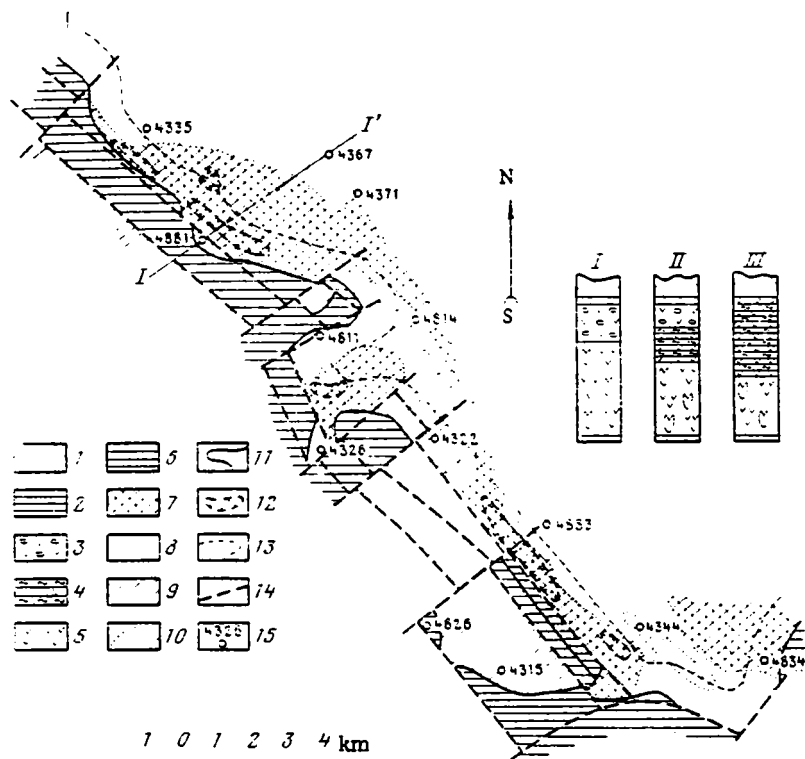


Fig. 1. Schematic lithofacies map of the Tirassk deposits in the Lisetsk exploration area (compiled by the authors and I. I. Gerasimova). 1) Overlapping sand-clay deposits of late Tortonian age (Kosovskaya suite); 2-5) deposits of the Tirassk suite (2, limestones of the Ratyn horizon; 3) nodular carbonate-sulfate rocks; 4, clay-sulfate rhythmites; 5, anhydritized coarsely crystalline gypsum with subvertical crystals); 6) lower Tortonian (Baranovsk) sandstones underlying the Tirassk suite; 7-9) lithofacies zones (7, type I section; 8, type II section; 9, type III section); 10) contact between lithofacies; 11) contact between stratigraphic units; 12) outline of metasomatic sulfur-ore calcitites; 13) outline of structural belt where sulfur deposits are likely; 14) fault; 15) exploratory drillholes with numbers.

Soviet Union, Poland, Rumania, and Yugoslavia. This formation was deposited in the Central Paratethys.

In the Soviet Carpathians, the upper Tortonian evaporite complex is included in the Tirassk suite, which is composed of a gypsum-anhydrite sequence together with metasomatic sulfur-bearing (sulfatic) carbonate rocks and sedimentary limestones of the Ratyn sequence. The Tirassk suite, overlapped by a thick sequence of terrigenous deposits, forms a continuous mantle over the outer zone of the Carpathian foothills foreland basin, approaching the surface along the southwest margin of the Eastern European platform, where erosional remnants (coarse and fine) of these deposits are found. The suite generally does not exceed 40 to 50 m in thickness, and increases to 250 m or more only in deep basins (Korshevsk, Zavolotovsk) as a result of the presence of soluble salts. The Tirassk suite is transgressive over lower Tortonian and older marine rocks.

The gypsum-anhydrite deposit in the Tirassk suite is generally regarded as a uniform sequence, formed during a single sedimentational cycle. According to a number of investigators [1, 4, 7], deposits of the Tirassk suite were formed in a shallow-water, lagoonal environment. Its huge area of distribution, clearly not in accord with the concept of a "lagoon," later led Strakhov [14] to conclude that the evaporites accumulated in a large, closed marine embayment of the Kara-Bogaz type. Investigations carried out over many years by the present authors

have enabled new data to be obtained on the paleogeographical conditions at the time of formation of the Tirassk suite.

Lithology and Facies of the Tirassk Suite. Study of the lithology of the Tirassk suite confirmed Kropacheva's ideas on the heterogeneity of its facies. Facies complexes formed in a sebkha environment can be recognized within the gypsum-anhydrite deposits of the Soviet Carpathians on the basis of textural features of the sulfates and a number of other indicators. The sebkha facies is distributed primarily in a narrow belt nearly parallel to the Carpathians, coincident with the basin-platform boundary. The sulfur deposits are localized within this belt. Subaqueous complexes of sulfates predominate outside the zone of the basin-platform boundary [13]. On the basis of studies of deposits of sulfates of the same age in Rumania, Khrushchov [15] also notes the widespread distribution of the sebkha facies in Tortonian evaporite formations of the Carpathians.

We have carried out studies of the lithology and facies of the sulfur-producing sulfate deposits in one of the areas of detailed sulfur exploration in the southeastern part of the Carpathian basin. The data obtained have been compiled on a small-scale derivative lithofacies map of the sulfate deposits (Fig. 1).

The Lisetsk study area is located in the transition zone between the platform and the outer zone of the Carpathian basin within the Maidan-Ivano-Frankosk transverse uplift. The structure is complex: the producing deposits of the Tirassk suite are cut by a series of faults that trend subparallel to the Carpathians, many of which have a throw of more than 100 m and are part of the Kalysh fault system. Transverse faults have considerably less displacement. The complex fault system results in block fault structure in this area. Deposits of the Tirassk suite, which are here 3-38.5 m thick, dip gently toward the adjoining Carpathian basin.

The area of study has been intensively drilled, so that the Tirassk section can be studied in detail and the morphogenetic types of sulfate rocks can be recognized. We previously developed this methodology [9], which is based on a classification of primary textures of sulfate and carbonate-sulfate rocks encountered in the sulfur workings.

Documentation of drill cores in the Lisetsk area shows that certain morphological types of sulfate-bearing beds can be traced over relatively large areas, in which they occupy a fixed position in the section, i.e., they pertain to a certain facies complex. They are considered microfacies by Ivanov and Voronova [3]. This suggests that they can be mapped, so auxiliary facies profiles were constructed along the line of drill holes. One of these profiles is presented in Fig. 2.

We will briefly dwell on the nature and depositional environments of the morphogenetic types of sulfate and carbonate-sulfate rocks encountered in the Lisetsk area.

Sulfate rocks with coarse-grained gypsum everywhere occupy the lower part of the gypsum-anhydrite section. They are not anhydritized or replaced by secondary gypsum after anhydrite. The primary texture is recognized by the nature of the vertically oriented elongated light patches, which are deformed pseudomorphs of later sulfate minerals after coarse, spiky, well-defined crystals of primary sedimentary gypsum, formed in quiet, shallow areas of the evaporite basin. These rocks average 10-15 m in thickness.

Thin interbeds of stromatolitelike forms are found within sulfate beds with coarsely crystalline gypsum. Such textures are inherited from primary biomorphic carbonates formed by blue-green algae. The stromatolites were sulfatized during early diagenesis, which thus resulted in sulfate rocks with characteristic stromatolite textures. The stromatolite-like rocks achieve a significance of their own along the northwest margin of the Lisetsk area, where such beds reach a thickness of 10-15 m, while a few thin interbeds of coarsely crystalline gypsum play a subordinate role.

Sulfate rocks with coarsely crystalline gypsum and stromatolites together form a single facies complex, developed on a shallow shelf.

Morphogenetic types of the productive beds also include clay-sulfate rhythmites and carbonate-sulfate rocks of porphyrite-like texture.

The rhythmites contain inclusions of clay in the form of very thin laminae, and as larger beds and lenses up to several centimeters thick. As a rule, the average thickness of the two-fold units (sulfate bed + clay layer) does not exceed 1 mm, and it probably represents an annual deposit with seasonal variation in composition. This type of rock occurs in relatively deep-water subaqueous facies complexes. In the evaporite horizon, such deposits are

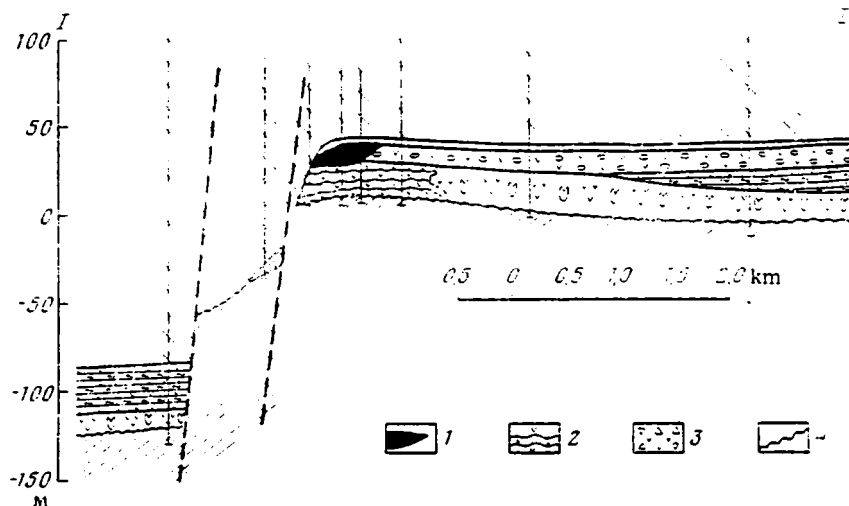


Fig. 2. Lithology and facies profile along I-I' (see Fig. 1).
1) Sulfur-ore limestones; 2) stromatolites sulfatized during diagenesis; 3) shelly sulfate rocks; 4) surface of erosion. See Fig. 1 for other standard symbols.

not found throughout but occur only in the middle and upper parts of the section. They range from 5 to 18 m in thickness.

The porphyrite-like carbonate-sulfate rocks are mainly nodular types. Oval sulfate nodules 1-5 cm in diameter occur in a limestone matrix. The carbonate content in these rocks varies widely (from 5 to 40%). These deposits are referred to a subaerial facies complex of ancient sebkhas [13]. In the study area they range from 2 to 9 mm in thickness. They are locally developed on uplifted blocks, where they cap the section of the productive beds.

The lithofacies study thus permits the Tirassk suite to be subdivided into various morphogenetic types. Analysis of environments of deposition makes it possible to recognize three facies complexes of sulfate deposits formed under different conditions:

1) nearshore shallow water complex, represented by an association of sulfate rocks with coarsely crystalline gypsum and stromatolites (littoral zone);

2) subaqueous, relatively deep-water complex (sublittoral zone), which includes clay-sulfate rhythmites; and

3) subaerial complex (supralittoral, nearshore carbonate sebkha), the main deposits of which are nodular carbonate-sulfate rocks.

In addition to sulfate and carbonate-sulfate rocks, pure carbonate rocks are also present in the Tirassk suite in the Lisetsk area. They are subdivided into two genetic groups. One of these contains sulfur mineralization which is attributed to metasomatism [5, 11, 12]. The second group consists of sedimentational limestones of the Ratyn horizon, up to 1 m thick, which are essentially devoid of sulfur mineralization. This group contains biochemogenic, algal, and other deposits accumulated in saline marine basins.

On the basis of the pattern of variability of the facies profiles of the upper Tortonian sulfates throughout the Lisetsk area, we have distinguished three types of sections of the Tirassk suite, located in separate areas of different extents and differing in the set and sequence of facies.

A twofold section is the *first type*. At the base it is anhydrite and gypsum with a primary, coarsely crystalline gypsum texture, and in the upper part, nodular carbonate-sulfate rocks. Areas with this type of section are limited in extent, and occur mainly along the uplifted side of the Kalush fault, which separates the outer zone of the basin from the barely submerged part of the platform.

The *second type* is characterized by a three-part section, in which layers of clay-sulfate rhythmites occur between a unit of rocks with nodular texture and a unit with coarsely crystalline gypsum texture. Zones with this type of section are located basically in the platform part.

The *third type*, as in the first, is twofold. Rocks with coarsely crystalline gypsum texture occur at the base. The upper part of the gypsum-anhydrite horizon is clay-sulfate rhythmites. The areas with this type of section are mainly within the more subsided blocks, but they are also found on uplifted blocks. The latter are associated mainly with post-sedimentational tectonic movements.

In accordance with the classification of the facies of the Tirassk suite on a geologic map, at a scale of 1:25,000, compiled by geologists of the Carpathian project, disregarding terrigenous deposits (Kosovskaya suite), we have recognized lithofacies zones in the Tirassk that correspond to one of the facies profiles (type of section).

On the schematic lithofacies map (see Fig. 1) the contacts between lithofacies zones were correlated with geologic map boundaries of synsedimentary tectonic structures (blocks), the relative ages of which we determined by analysis of thickness and measured sections. These factors in turn permitted us to refine the boundaries of the tectonic elements which had previously been located by geologists of the Carpathian project from geophysical and general geologic data.

Paleogeographic Conditions of Formation of the Tirassk Suite. On the basis of the lithofacies map and the facies profiles set up, it has become possible to reconstruct the environments of deposition in the Lisetsk area during Tirassk time. We have compiled schematic paleogeographic maps at a scale of 1:50,000 for the various stages of sedimentation of the gypsum-anhydrite horizon (Figs. 3-5).

Three basic stages can be recognized in the evolution of the evaporite basin from the facies analysis.

In the first stage (see Fig. 3), transgression over the ancient, erosional land surface of pre-Tirassk age took place. Coarsely crystalline gypsum with subvertically oriented crystals, often with associated biochemogenic carbonate sediments, were deposited in a shallow saline environment after migration of the shore line. The gypsum crystals grew either in some subaqueous substrate or in a dry, subaerial carbonate and clayey carbonate mud. In the tidal zone, and in subaerial environments of the mudtidal zone, the growth of stromatolitic bioherms, which would be partly or completely sulfatized during early diagenesis, took place simultaneously. In sublittoral areas far from shore in the open evaporite basin, below the zone of photosynthesis and wave base, seasonal clay-sulfate rhythmites were deposited. The source of the clay was intensive erosion of Carpathian rocks [1].

During middle Tirassk time the region experienced structural activity and corresponding changes in depositional environment (Fig. 4), which were related to the next stage of subsidence of the outer zone of the basin, beginning in lower Tortonian time [2]. Movement along the Kalush fault resulted in division of the sedimentary basin into two parts. Land areas located to the southwest of the fault, and the adjacent part of the basin, began to subside actively. Relatively deep-water clayey-sulfate rhythmites were deposited here. Along the northeastern side of the fault a series of anticlines formed (see Fig. 4). The cores of these folds often rose above the water level, creating a chain of low islands surrounded by shallow-water banks. Biochemogenic carbonates accumulated on these shoals.

A unique tidal flat (sebkha) was formed on the low-lying land areas. Coastal areas along the Persian Gulf are modern analogs [8]. As a result of intensive capillary evaporation of groundwater, which was supplemented by the evaporite basin, subaerial growth of gypsum nodules or discrete lenses of gypsum crystallites began in carbonate sediments previously deposited or washed in by storms. In this process, carbonate sediments were mechanically expanded and partially replaced by gypsum, which produced the mixed carbonate-sulfate rocks with a porphyrylike texture.

The carbonate fraction of these mixed rocks is commonly represented by the products of organic activity of blue-green algae, found in tidal flats as algal mats in the pore spaces of which gypsum has crystallized. Numerous coprolites can sometimes be seen in the carbonates, which indicates vigorous development of a euryhaline fauna in waters of the adjacent saline basin.

In addition to the nodular texture of the carbonate-sulfate rocks, the presence of flat-pebble conglomerates also is an indicator of deposition in a tidal-flat environment [8]. These are formed in agitated waters of a beach zone by disruption of previously deposited, weakly lithified carbonate and sulfate sediments. An abundance of redeposited clastic rocks,

including flat-pebble conglomerates, is a general characteristic of the Lisetsk area, which indicates frequent subaerial exposure of the littoral depositional zone during periods of intraformational discontinuities.

However, along with subaerial deposition of carbonate-sulfate sediments, beyond shallow-water and island barriers isolated lagoons were formed on the platform during maximum transgression. Here, in relatively quiet conditions with low wave dynamics, thinly laminated sediments, composed of either sulfate minerals alone or rhythmic interlamination of clays and sulfates, began to form.

In slopes along the bottom of the basin adjacent to the Kalush fault, frequent movements took place which caused underwater landslides of weakly lithified sediments. Breccias were thus produced which were composed of fragments of sulfate rocks of various origins, including those redeposited from the beach zone. The breccias formed trains or debris cones on and at the base of submarine slopes in deep, basinward areas. The Tirassk section is locally almost totally composed of these breccias. The breccia clasts are generally rounded. The cement is mostly carbonate-sulfate or clay-carbonate-sulfate. The breccias form well expressed lenticular bodies and interbeds, concordant with bedding, in the section.

In the concluding stage of sulfate deposition (see Fig. 5) gradual regression of the evaporite basin began. Since the average thickness of the seasonal rhythmite doublets (clay-sulfate laminae) was shown to be at the rate of 1 mm/yr, then from the maximum thickness of the rhythmite section in the lagoonal zone of about 8 m we may assume a period of 6-8 thousand years of rhythmite deposition in this area of the irregular bottom of the basin.

From the rate of accumulation of the clay-sulfate rhythmites, we can calculate the time of deposition of the entire section of the Tirassk suite in the study area. The thickness of the suite in the deepest part, composed entirely of clay-sulfate rhythmites, is 30-40 m. Since no interruption in sedimentation is found in the sublittoral zone, we may then assume that the whole sedimentational cycle lasted approximately 40 thousand years. It is quite likely that deposition of the gypsum-anhydrite section in other areas of the upper Tortonian evaporite basin took about the same amount of time.

Upon further regression, broad sebkha plains were formed in lagoonal areas, as well as on carbonate banks and islands. These were periodically inundated, during maximum high tides, and strong storms. Mixed carbonate-sulfate deposits with porphyrylike texture accumulated here in subaerial conditions. Sedimentation of only a few clay-sulfate rhythmites continued in the depressed southwestern part of the Lisetsk area.

The end of Tirassk time was marked by limited distribution of water in the evaporite basin. Sulfate deposition was replaced by sedimentation of carbonates of the Ratyn horizon [1, 11]. This involved deposition of clayey, pelitomorphous limestones in the deeper part of the basin, with highly saline water, and biochemogenic limestones with traces of algal activity, numerous coprolites, and fine crystallites of gypsum, replaced by secondary calcite during early diagenesis, in the uplifted parts. Consequently, an arid tidal flat environment is preserved here.

The subdivision of the Tirassk suite into layers corresponding to microlithofacies of sulfate deposits makes it possible to reliably identify erosion surfaces, both within the suite and on its upper surface, which are associated in many cases with sharp variations in thickness of the deposits in the study area. Between stacked microlithofacies, in areas where the thickness of individual layers is preserved or completely collapsed, erosional contacts are seen with karstic sinks and caverns filled with fragments of sulfate and carbonate rocks. Apparently indications noted in the study area of both intraformational erosion and erosion of the top of the gypsum-anhydrite horizon in pre-Kosov or early Kosov time are characteristic not only of the southeastern part of the basin but over the entire sulfur-bearing region, which was observed earlier by other investigators as well [10].

Thus the paleogeographic conditions during deposition of the Tirassk suite were complex and were characterized by frequent changes in the depth of the basin. At certain times, especially at the conclusion of the formation of the sulfate sequence, there was a tidal flat where carbonate-sulfate sediments accumulated in subaerial conditions. At the same time, localities with submarine, relatively deep-water deposition of thin-bedded sulfates and clay-sulfate rhythmites existed in areas of the outer zone of the basin.

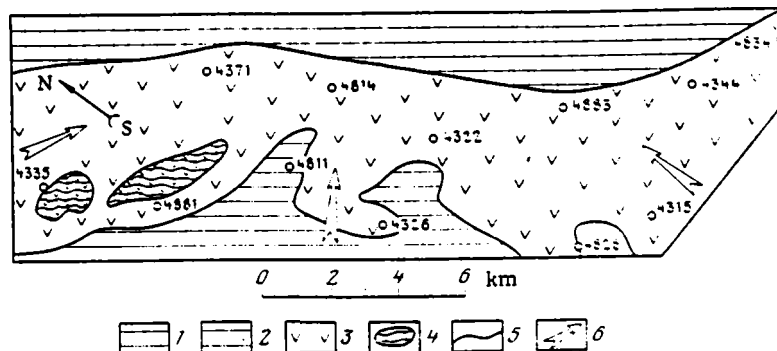


Fig. 3. Paleogeographic diagram of gypsum-anhydrite deposition in the Lisetsk area during early Tirassk time. 1) Land area; 2) sublittoral zone; 3) littoral zone; 4) stromatolitic bioherm in the littoral zone; 5) contact between zones of different sedimentary environments; 6) direction of marine incursion. Other environments indicated on Fig. 1.

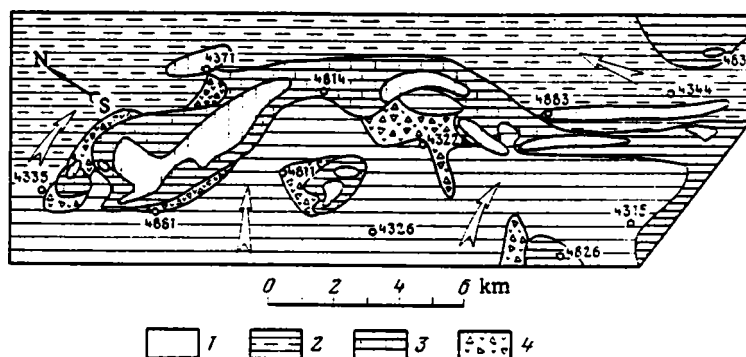


Fig. 4. Paleogeographic diagram of gypsum-anhydrite and carbonate deposition in the Lisetsk area during middle Tirassk time. 1) Supralittoral-paleosebkha zone; 2) lagoonal zone; 3) shallow-water biochemogenic carbonate zone; 4) zone of accumulation of sedimentational breccia at the foot of submarine slopes. Other environments shown on Figs. 1 and 3.

Effect of Lithofacies Composition of the Tirassk Suite and Its Paleogeographic Conditions of Formation on the Localization of Sulfur Deposits. The outlines of six small ore bodies discovered during exploration are presented on lithofacies and paleogeographic diagrams (see Fig. 1, 5). These are based on new lithologic factors effecting the distribution of sulfur deposits that can be used as exploration criteria.

It has been shown that ore bodies are located only in zones with the first type of facies profile. The presence in the upper part of the Tirassk suite of relatively permeable subaerial carbonate-sulfate rocks with nodular texture is characteristic of this type. Metasomatic alteration, which formed the sulfur deposits, takes place in these rather than in pure sulfate and clay-sulfate rocks, which are effective fluid barriers [13].

Ores originating in carbonate-sulfate rocks with nodular texture occupy the same hypsometric level as rocks of the substrate from which the metasomatic alteration proceeded. The northwestern part of the area, where ore was formed in relatively permeable stromatolites, sulfatized during diagenesis, is an exception. This ore occurs in the upper part of the section of the productive sequence, and is the result of erosion of nodular rocks which had previously occupied the upper part of the section.

In areas where the relatively permeable carbonate-sulfate rocks are absent (lithofacies zones with sections of the third type), sulfur deposits are not formed. The clay-sulfate rhythmites, located in the upper part of the sequence, have undergone essentially no metasomatism because of limited permeability. Even in zones with the second type of section, however, where the upper part of the Tirassk suite is occupied by the relatively permeable carbonate-

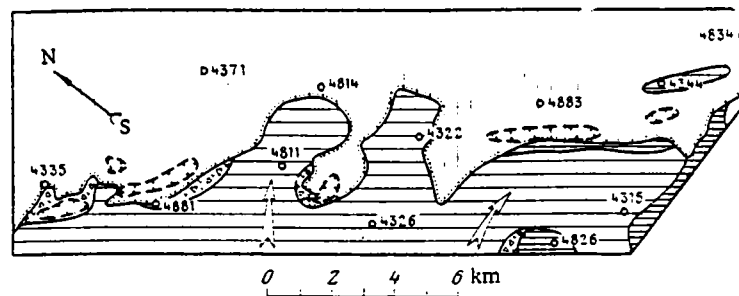


Fig. 5. Paleogeographic diagram of gypsum-anhydrite deposits during late Tirassk time. Environments shown on Figs. 1, 3, and 4.

sulfate rocks, but clay-sulfate rhythmites are present in the middle of the section, no metasomatic alteration has taken place and no ore formed. This is because of the negative role of the clay-sulfate rhythmites, which in any part of the section block the dissemination of the solutions (fluids) necessary for sulfur-forming reactions.

Structural patterns are also important in the analysis of the distribution of sulfur deposits in the Lisetsk area. All of the sulfur deposits are located in a narrow belt adjacent to the zone of complete erosion of the Tirassk suite with exposure of the pre-Kosov Cretaceous and lower Tortonian sandstones.

The restriction of the sulfur deposits in the study area to this zone is, in our opinion, shown by two factors: 1) the favorability of the pinchout zone of sulfate rocks for intensive infiltration of ore-forming solutions to the place of sulfur-forming reactions from this "window" in the evaporite sequence; and 2) the coincidence of this zone with large-amplitude (50-100 m) structures, which can be considered to be ore-controlling. Other investigators [10, 16] have also directed their attention to the location of sulfur deposits along the line of pinchout of the Tirassk suite within a distance of 0.5-1 km, so this factor is considered one of the leading ones for exploration at the present time.

We will consider the nature of the location of areas in the Lisetsk region with various types of lithologic facies sections within the narrow, kilometer-wide belt along the pinchout of the Tirassk suite, which is the most prospective zone for sulfur. This belt extends for 43 km, and contains frequent alternation of areas with various facies types, which is due to paleogeographic conditions at the time of deposition. This feature is due to the dissected nature of the shore line, which in the last stages of Tirassk time was divided into littoral and supralittoral areas (see Fig. 5). In Fig. 1 it can be seen that in the kilometer-wide belt where sulfur deposits are likely, four small areas with the first type of Tirassk section, in which sulfur deposits are possible, alternate with areas in which the rocks are not favorable for sulfur-forming metasomatic processes. This facies variability of the productive sequence in the structural belt of potential ore development served as an obstacle to the formation of major sulfur deposits of the Lisetsk area.

The relationship between lithologic facies of the productive rocks and the intensity of sulfur-forming processes is borne out in several other areas in the Carpathian basin.

Our lithofacies studies in the areas of the Zagoipol'sk and Shevchenkov deposits has shown that the makeup of the lithofacies zones is similar to that of the Lisetsk area. Significant differences in their extent are found, however.

Both of these deposits are located on the borders of the Zabolotov basin, the axial portion of which is composed of either rocks of the third type of lithofacies zone or entirely of relatively deep-water, thin-bedded anhydritized gypsum interbedded with halite containing clay impurities. Because of this the Zabolotov basin is not likely to have sulfur deposits, which has been confirmed by drilling.

On the two opposite margins of the basin, where the Shevchenkov and Zagoipol'sk deposits are located, the first type of lithofacies is most widespread; zones with the second type occur in the area of the deposits, where we have studied them in the greatest detail at the Shevchenkov deposit; zones of the third type are not present. These zones are small, and ore has not been found in them. Such areas are like "windows" in the sulfur deposits.

Consequently, the relatively small areas occupied by zones of the second lithofacies type, in the complete absence of the third type and the widespread distribution of the first type, are favorable places in the kilometer-wide belt along the Tirassk pinchout for the formation of commercial deposits of sulfur on the margins of the Zabolotov basin.

The lithofacies profile we have previously constructed along the strike of the Grimov sulfur deposit [13] also attests that, along with other factors, the absence of clay-sulfate rhythmites below areas of localization is a favorable lithologic condition. Their presence in the productive section signals the appearance of the second and third lithofacies types and is an unfavorable factor in sulfur deposition in those places.

Lithofacies analyses we conducted earlier on one of the deposits of the Gaurdak-Kugitang region [6] also confirm that under various other conditions the processes of sulfur formation are selected according to facies type in zones that are structurally favorable.

Thus, without excluding other factors that may have made metasomatic sulfur formation possible (tectonic, geochemical, etc.), the authors wish to stress the need for consideration of the lithologic facies of the productive beds and the paleogeographic conditions of formation in the search for sulfur. Lithologic facies studies early in the geologic surveying and general exploration for sulfur makes it possible to evaluate prospective localities in the study area according to lithologic factors.

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LITHOLOGIC AND PETROPHYSICAL STUDY OF ANTHRACITE DEPOSITS IN THE DONETS BASIN

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Results of a study that utilized new geological-geophysical methods in the investigation of drillhole sections are presented. It greatly enhanced capabilities, used in subdividing anthracite-bearing terrigenous deposits, providing great refinement in details. Detailed petrographic and lithophysical characteristics are presented for the first time in subdividing types of anthracites and their enclosing rocks, their composition and geochemical makeup, physical characteristics and areal distribution in Donets Basin deposits.

The Donets Basin is the main anthracite supplier of the country. Presently 135 mines produce 70.6 millions tons of anthracite; c. 35% of the mined coal in the Basin. In terms of area to be excavated by mining, anthracites represent c. 25% of the coal deposit area of the Basin but these reserves are only c. 22% of the total coal reserves (Fig. 1).

Anthracites are not only an energy source [1]. They are also utilized in various technologies, as in foundries and electorde production, for Ca-carbide, Si-carbide, thermoanthracite, synthetic corundum production and bauxite sintering. The Donets Basin anthracites play an important part in these industries, as, for instance, thermoanthracite is produced only from anthracites of this basin and thermographite is obtained only from certain beds of Donets Basin anthracites [5].

The basis for solving all geochemical tasks lies in lithological identification. Until now, this was done by visual examination of drill cores from exploration holes. Due to the incomplete core recovery, this kind of documentation does not result in full documentation of all the rock units and their depositional sequences in the drillhole section.

Prevailing geological methods (petrographic work, various laboratory tests and analyses) provide a full and complex system of rock identification. However, considering limitations in laboratory efficiencies, in the number of specialists and the enormous number of drill samples, such studies cannot be performed throughout the section of each exploration hole.

A complex of geophysical methods (GIS) is presently employed in coal exploration, recording a whole set of physical characteristics from each bed: porosity (K_p), specific electric resistivity (ρ_p), intensity of natural gamma radiation (I_γ), volume density (δ_N), acoustic characteristics (longitudinal and transverse wave propagation velocities; v_p and v_s , respectively, as well as the energy attenuation of ultrasonic oscillations, α) the effective atomic number of the medium (z_{ef}), and diameter changes of the drillhole during drilling, d_s .

These physical characteristics are caused by the geophysical rock properties (mineral composition, grain size, epigenetic alteration grade, etc.). This allows detailed lithologic studies, based on geophysical data.

However, geophysical methods in practice are not used in solving problems. Currently, the geophysical survey subdivides the anthracite deposit sections by using geophysical diagrams qualitatively. Only a limited number of basic lithotypes are identified (clayey shales, sandstones, limestones, and coals), without definition of their composition and identifying intermediate lithological varieties. Such subdivision is based on relative changes in the apparent values of measurable physical rock parameters and detaching them from geological data. This has a negative effect on the efficient use of geophysical information. In addition, the petrophysical characteristics are not completely taken into consideration.

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Thus, for practical purposes, neither the geological nor geophysical methods provide answers to satisfy the increased demands of the coal industry. Sufficient details and breadth is needed in the study of the lithology and composition of rocks in the investigated mine region [7].

To completely satisfy this task with maximum efficiency, a total determination of all organic compounds is needed and use of all the potential of geological and geophysical methods; a complex geological-geophysical approach in the study of coal-bearing deposits. This method was developed and proven [2] in coal deposits of the Pechora, Donets and Kuznetsk Basins [3, 4, 6].

The method was not developed in anthracite deposits. As earlier petrophysical studies [2, 4] have shown, the anthracite-bearing coal deposits display a number of unique geological and geophysical features, in contrast with coal-bearing sediments. For this reason, specific geological-geophysical studies are required in anthracite beds, as shown in the present paper.

Work on semianthracite and anthracite deposits was conducted in three regions of the Donets Basin: (1) Chistyakov-Snezhnyansk area; (2) Sulina-Sadkinsk area; and (3) the Dolzhensk-Rovenetsk area (part of the mine named for the 23rd Congress of the CPSU). This mine area will be called now for brevity, "mine area No. 1." Designations of rock changes and coal metamorphism follow those of Grechukhin [2].

The geological-geophysical method is a complex of detailed geophysical, lithological, petrophysical, chemical and other studies, used in drillholes with uniform parameters, with effective use of the geophysical drillhole study method (GIS) in all exploration holes in the region for solving the problems. The maximum use was made from the petrophysical patterns of coal-bearing deposits.

IDENTIFICATION OF PETROLOGICAL ROCK TYPES IN DRILLHOLE SECTIONS IN DETERMINING ROCK COMPOSITION ANTHRACITE-BEARING COAL MEASURES

Unequivocal correlation of physical rock parameters with their composition characteristics has been demonstrated in individual intervals of coal-bearing units. These were designated as lithological-geophysical stages within the vertical sections, and as lithological-geophysical zones, in terms of areawide locations (Table 1).

The studies have shown that the coal-bearing sedimentary rocks contain three components: clayey (S_{g1}), carbonate (S_k), and clastic (S_{k1}) matter.

Comparison of geophysical and geological data from the selected drillholes allowed a quantitative correlation between geological characteristics and petrophysical parameters of the rocks (Tables 2 and 3). Figure 2 illustrates these relationships. Laboratory analysis data from core samples provided petrographical categories and allowed definition of the geochemical rock characteristics (Fig. 3). Based on these interrelationships, a triangular diagram was developed. The sides of the triangle represented rock composition, in terms of clastic, clayey and carbonate components (Fig. 4). A dot corresponds to a given composition in the diagram. Dots, representing known composition, granulometry, and physical parameters of a given rock unit are plotted on the diagram. Isolines of the physical parameters have been constructed next.

The diagram is used in determining rock composition, based on geophysical data in a section, displaying lithological-geophysical stages. One plots composition-dots, representing physical parameters, measured in the drillhole in the section within the studied rock unit. The data provide isolines of the physical rock characteristics. These isolines are intersected at one point or form a polygon of uncertainty. The point of isoline intersection or the polygon center in the coordinates of the triangular diagram provides values of the physical characteristics of the bed and its composition in terms of clastic, clayey and carbonate matter. It also describes the predominant size of detrital grains [2, 6].

Petrophysical and compositional characteristics (Table 4 and Fig. 5) and also values on the triangular diagram (Fig. 6) are defined for each lithological-geophysical stage in the coals and coal-bearing rocks with 10-100% organic composition. Sides of this triangular diagram represent axes of coal composition; representing organic, clay and clastic matter.

All coal-free rocks are classified according to carbonate composition in the following groups: rocks with clay cement ($S_k = 0-10\%$), with clayey-carbonate cement (10-25%), with

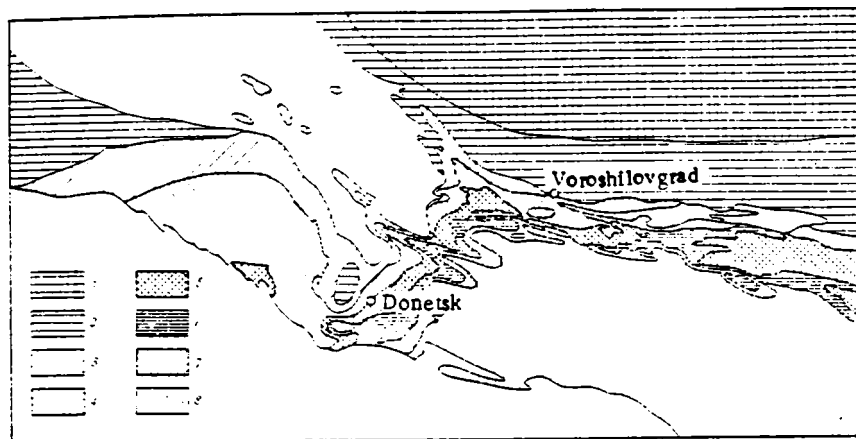


Fig. 1. Area distribution of metamorphosed coal types on the Carboniferous surface (the metamorphic group boundaries established by M. L. Levenshtein, except between BD-B₃). Metamorphosed coal categories: 1) bright brown (B₃); 2) transitional between brown and long-flame coals (DB); 3) long-flame (D); 4) gas coals (G); 5) bituminous, coke coal, lean cannel-clinker coals (Zh, K, OS); 6) bed (T); 7) semianthracites (PA); 8) anthracites (A).

TABLE 1. Dimensions of Lithological-Geophysical Grades of the Composite Petrophysical Section of Deposits with Anthracite Content

Position of an interval in the composite petrophysical section			Lithological-geophysical grade, m;	Change in physical characteristics, based on main lithotope			
alteration stage		depth of maximum burial, m;		K _n , %	σ _N , kg/m ³	v _p , m/sec	ρ _p , g/cm
number	index						
XIII	PA ₁	6 250	250	0.07	3	25	80 (32)
XIII	PA ₁	6 500	250	0.07	3	25	70 (28)
XIV	PA ₂	7 000	500	0.13	5	50	100 (20)
XV	A ₁	7 500	500	0.13	5	50	75 (15)
XVI	A ₂	8 000	500	0.13	5	50	75 (15)
XVII	A ₃	8 650	650	0.17	6	65	100 (15)
XVIII	A ₄	9 400	750	0.20	7	75	110 (15)
XIX	A ₅	10 000	600	0.16	6	60	90 (15)

Note. The main parameter is δ_p ; the main lithotype: sandstone; the K_p gradient per 100 m: 0.03%; for δ_N : 1, for v_p : 10, for δ_p : given in brackets.

carbonate cement (25-50%), carbonate rocks and limestones with terrigenous admixture (50-75%), carbonate rocks and limestones (75-100%). The detrital rock groups are subdivided into subgroups, based on the dominant grain size (d_s , in mm): 0.05-0.10; 0.10-0.25, 0.25-0.50, 0.5-1.00; and clayey rocks, based on the detrital content: 0-25 and 25-50%.

The classification results in the distinction between various lithotypes, based on granulometry, composition and physical characteristics (Table 2, Fig. 2). Coals and coal-bearing rocks were subdivided according to organic matter content, as follows: clayey shales, low coal content (C_{org} = 10-20% organic composition), medium coal content (20-35%), high coal content (35-50%), high-ash anthracite (50-70%), medium ash content anthracite (70-85%) and low ash content anthracite (85-100%).

The rock types, quantitatively displayed granulometrically (one indicator), compositional (3 indicators), geochemical compositional (14 indicators), petrophysical (8 indicators), and epigenetic (2 indicators; stages and grades) characteristics. Altogether 28 indices have been considered and a petrophysical (lithological) designation given to the types [2]. This petrophysical type, in contrast with the lithological type (lithotype) is needed in studying the strength, deformational, structural, engineering, physical-mechanical characteristics, and stability of coal-bearing rocks [7].

TABLE 2. Petrophysical Characteristics of Lithotypes in

Petrographic type					
Number	designation	dominant fragment size, in mm	composition, %		
			clayey cement	carbonate cement	clastic matter
I	Conglomerate	>1.0	0—12	0—10	85—97
II	Sandstone, coarse-grained, with carbonate cement	0.50—1.0	0—7	10—25	75—90
III	Sandstone, coarse-grained, with clayey cement	0.50—1.0	0—12	0—10	84—95
IV	Sandstone, medium-grained, with carbonate cement	0.25—0.50	0—10	25—50	48—74
V	Sandstone, medium-grained, with carbonate-clayey cement	0.25—0.50	0—14	10—25	67—83
VI	Sandstone, medium grained, with clayey cement	0.25—0.50	7—17	0—10	77—88
VII	Sandstone, fine-grained, with carbonate-clay cement	0.10—0.25	3—23	25—50	35—65
VIII	Sandstone, fine-grained, with clayey-carbonate cement	0.10—0.25	10—28	10—25	53—77
IX	Sandstone, fine-grained, with clayey cement	0.10—0.25	15—30	0—10	63—83
X	Shale, aleurolitic-carbonate, clayey	0.05—0.10	15—42	25—50	20—50
XI	Shale, aleurolitic-clayey-carbonate	0.05—0.10	23—50	10—25	35—53
XII	Shale, aleurolitic-clayey	0.05—0.10	28—55	0—10	40—70
XIII	Shale, carbonate-clayey-aleurolitic	0.01—0.05	30—58	25—50	10—34
XIV	Shale, clayey-aleurolitic-carbonate	0.01—0.05	42—68	10—25	18—40
XV	Shale, clayey-aleurolitic	0.01—0.05	50—75	0—10	22—45
XVI	Shale, clayey-carbonate	<0.01	40—75	25—50	0—17
XVII	Shale, clayey-carbonate	<0.01	60—90	10—25	0—22
XVIII	Shale, clayey	<0.01	68—100	0—10	0—25
XIX	Carbonate rock, sandy (concretions)	0.10—0.25	0—15	50—75	18—50
XX	Carbonate rock, aleurolitic (concretions)	0.05—0.10	7—30	50—75	10—35
XXI	Carbonate rock, clayey-aleurolitic (concretions)	0.01—0.05	15—40	50—75	3—20
XXII	Carbonate rock, clayey (concretions)	<0.01	22—50	50—75	0—10
XXIII	Carbonate rock (concretions)	0.01	0—25	75—100	0—25
XXIV	Limestone, sandy	0.10—0.25	0—15	50—75	18—50
XXV	Limestone, clayey-aleurolitic	0.05—0.10	7—30	50—75	10—35
XXVI	Limestone, clayey-aleurolitic	0.01—0.05	15—40	50—75	3—20
XXVII	Limestone, clayey	<0.01	22—50	50—75	0—10
XXVIII	Limestone	0.01	0—25	75—100	0—25

Portions of Mine No. 1

Petrographic characteristics				Ratio in the section, %	
color	grain size	structure	cement type	in terms of thickness of units	in terms of number of beds
Variegated	Pebbly	Massive	Pore	0.1	0.1
Gray	Sandy	"	Pore, basal-pore	0.1	0.1
Light gray-to-white		Layered, massive	Pore	1.3	2.2
Gray	"	Massive, hidden bedding	Pore-basal, basal, corrosional	0.1	0.1
Light gray	"		Basal-pore corrosional	0.6	0.7
Light gray-to-white	"	Same	Pore	4.5	5.7
Gray	Sandy-sandy-aleurolitic	Massive indistinct layering	Basal corrosional	1.0	1.5
Gray, light gray	Same	Layered, massive	Pore-basal, corrosional	1.2	2.0
Same	"	Same	Pore, basal-pore	12.3	17.8
Gray	Aleurolitic,	Layered, indistinct layering	Basal corrosional	0.3	1.0
"	"	Same	Pore-basal, basal, corrosional	0.5	2.2
"	"	"	Pore-basal, basal-pore	16.5	21.0
"	Aleurolitic, aleurolitic-pelitic	Massive layered	Basal, corrosional	0.3	0.5
Gray, dark gray	Same	Layered indistinct layering	Same	1.1	1.1
Same	"	Thinly layered, indistinct layering	Basal, pore-basal	44.3	25.0
"	Pelitic		Basal, corrosional	0.2	0.4
Dark gray	"		Same	0.8	0.8
Dark gray to black	"	Same	Basal	9.9	9.7
Light gray-to-white	Sandy	Massive	Basal, corrosional	0.1	0.2
Gray	Aleurolitic	"	Same	0.1	0.2
"	Aleurolitic, pelitic, microgranular	"	Basal	0.2	0.3
Gray to dark gray	Microgranular, pelitic	"	"	0.2	0.3
Gray	Microgranular	"	"	0.7	0.8
"	Microgranular, sandy	Massive indistinct layering	"	0.1	0.1
"	Microgranular, aleurolitic	Same	"	0.1	0.2
Gray	Microgranular, aleurolitic	Massive	Basal	0.2	0.3
gray to dark gray	Microgranular pelitic	Same	"	0.2	0.3
gray	Microgranular	Massive indistinct layering	"	1.0	1.0

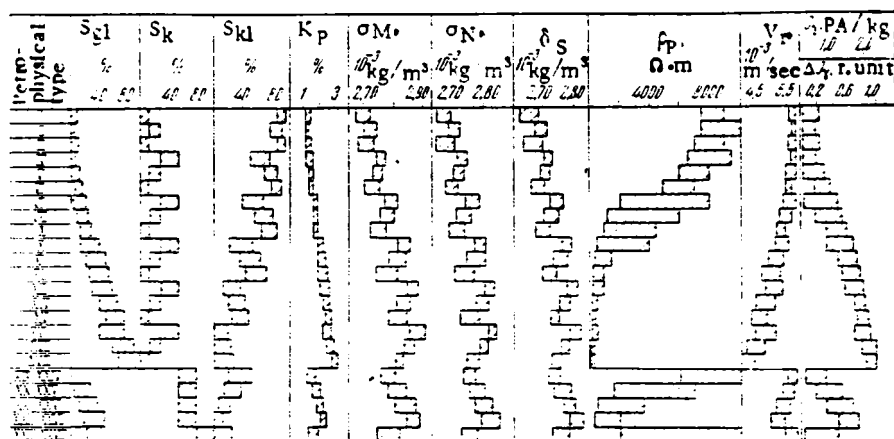


Fig. 2. Composition and physical characteristics of rocks in the anthracite deposits (in this and the following illustrations the metagenetic rock stage: XIX (A₉); the lithological-geophysical stage: VIII) Composition symbols S_{kl}, S_{gl}, S_k, represent clastic, clayey and carbonate content. Physical rock features: K_p) total porosity; δ_M, δ_N, δ_S - mineralogical, water-saturated, and dry rock densities, respectively; ρ_p) specific electric resistance; v_p) propagation velocity of elastic longitudinal waves; ΔI_γ) relative intensity of natural gamma radiation. Petrophysical type designations: Table 2.

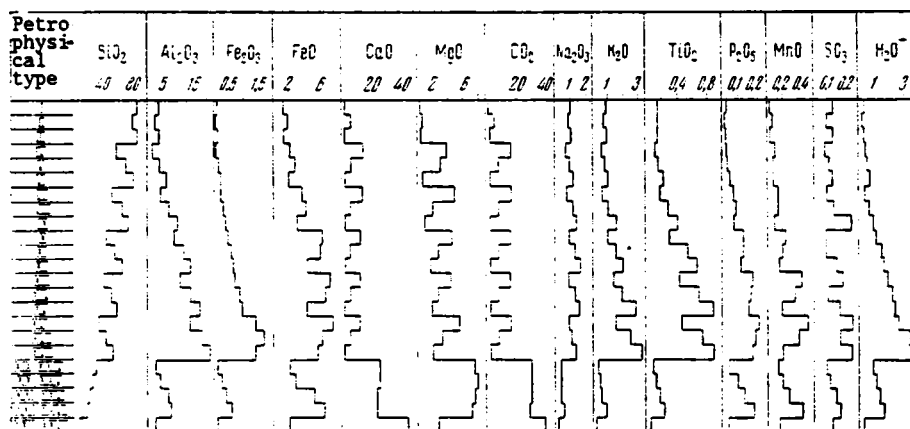


Fig. 3. Geochemical characteristics of petrophysical types of coal-bearing rocks (components in percentages). Petrophysical Category designations: Table 2.

LITHOLOGICAL-GEOPHYSICAL CLASSIFICATION OF DEPOSITS THAT ENCLOSE THE ANTHRACITE SEQUENCE

Part of the area of Mine No. 1 has been selected to characterize deposits with anthracite coals. All noncoal rocks have been subdivided into 28 petrophysical categories, defined by indices of granulometric, compositional, and chemical compositional features, physical characteristics, epigenetic conditions, rock color, structure, texture and cement type properties. Anthracite and carbonaceous shales have been subdivided into six lithotypes. Thus, altogether 34 lithotypes have been defined (Tables 2-4; Figs. 2, 3, and 5).

The mentioned characteristics together define the lithological-geophysical basis for rock and coal classification in the anthracite-bearing Donets Basin deposits. The example of lithological-geophysical stage VIII was selected in parts of Mine No. 1 in this process. The petrophysical types, representing more than 50% of the carbonates carry a binary numbering system, due to the different genetical backgrounds of these rocks (Fig. 2). For instance, aleurolitic limestone (Lithotype XXV) was the product of sediment-genesis, but aleurolitic carbonate rock

TABLE 3. Petrophysical Characteristics of Anthracite-Bearing Deposits in Parts of Mine No. 1

No. of litho- logic types	Total porosity, K _p , %	Density, 10 ⁻³ kg/m ³			Specific electric resistance, ρ _p , Ω·m	Propagation velocity of elastic longitudinal wave waves, v _r , 10 ⁻³ m/sec	Natural radioactivity	
		mineralogical, δ _M	water saturates rocks volume, δ _N	volume of ab- solutely dry rocks, δ _S			I _γ , pA/kg	ΔI _γ , rel. units
I	1,1-1,3	2,67-2,72	2,64-2,69	2,62-2,68	7 500-10 000	5,6-5,9	0,3-0,7	0,05-0,25
	1,2	2,69	2,67	2,66	8 200	5,8	0,5	0,15
II	1,1-1,3	2,70-2,74	2,68-2,72	2,67-2,71	7 500-10 000	5,7-5,9	0,3-0,6	0,05-0,20
	1,2	2,72	2,70	2,69	8 200	5,8	0,4	0,10
III	1,1-1,4	2,68-2,73	2,64-2,70	2,63-2,69	7 000-9 000	5,6-5,9	0,3-0,7	0,05-0,25
	1,2	2,70	2,68	2,67	7 400	5,8	0,5	0,15
IV	1,1-1,6	2,73-2,77	2,71-2,74	2,70-2,73	6 500-9 500	5,7-5,9	0,3-0,7	0,05-0,25
	1,4	2,75	2,72	2,71	8 200	5,8	0,4	0,10
V	1,3-1,6	2,73-2,77	2,70-2,74	2,69-2,73	6 000-8 000	5,5-5,9	0,3-0,9	0,05-0,35
	1,4	2,75	2,72	2,71	7 000	5,7	0,6	0,20
VI	1,3-1,6	2,70-2,75	2,67-2,71	2,66-2,70	5 000-7 000	5,5-5,7	0,6-1,0	0,20-0,40
	1,5	2,72	2,69	2,68	5 700	5,6	0,8	0,30
VII	1,6-1,9	2,77-2,81	2,74-2,78	2,72-2,76	2 000-8 000	5,4-5,9	0,4-1,1	0,05-0,50
	1,7	2,79	2,76	2,74	5 500	5,6	0,8	0,30
VIII	1,6-1,9	2,75-2,80	2,71-2,76	2,70-2,75	1 200-6 000	5,3-5,7	0,6-1,2	0,20-0,55
	1,7	2,77	2,74	2,72	3 300	5,5	1,0	0,40
IX	1,6-1,9	2,72-2,77	2,68-2,73	2,67-2,72	1 000-4 500	5,2-5,5	0,9-1,3	0,35-0,60
	1,7	2,74	2,71	2,69	1 850	5,4	1,1	0,50
X	1,8-2,3	2,81-2,85	2,77-2,80	2,76-2,79	600-4 000	5,1-5,6	0,9-1,5	0,35-0,70
	2,0	2,83	2,79	2,77	1 400	5,4	1,2	0,55
XI	1,9-2,4	2,78-2,84	2,74-2,80	2,73-2,78	500-1 500	4,9-5,4	1,1-1,6	0,50-0,75
	2,1	2,82	2,78	2,76	800	5,2	1,4	0,65
XII	1,9-2,5	2,74-2,81	2,70-2,76	2,69-2,74	450-1 000	4,7-5,3	1,2-1,7	0,55-0,80
	2,2	2,77	2,73	2,71	600	5,0	1,5	0,70
XIII	2,0-2,6	2,84-2,88	2,80-2,83	2,77-2,81	400-1 000	4,8-5,4	1,2-1,7	0,55-0,80
	2,4	2,86	2,81	2,79	600	5,1	1,5	0,70
XIV	2,3-2,7	2,81-2,85	2,77-2,81	2,75-2,78	350-600	4,5-5,1	1,5-1,8	0,70-0,85
	2,5	2,83	2,79	2,76	450	4,8	1,7	0,80
XV	2,4-2,8	2,78-2,84	2,72-2,78	2,72-2,75	300-500	4,4-4,9	1,6-1,8	0,75-0,90
	2,6	2,80	2,75	2,73	380	4,6	1,7	0,80
XVI	2,2-2,8	2,85-2,90	2,81-2,84	2,78-2,82	300-700	4,5-5,2	1,5-1,8	0,70-0,90
	2,5	2,88	2,83	2,81	400	4,9	1,7	0,80
XVII	2,5-3,0	2,83-2,86	2,78-2,81	2,75-2,78	230-400	4,2-4,8	1,7-1,9	0,80-0,97
	2,8	2,84	2,79	2,76	320	4,5	1,8	0,90
XVIII	2,8-3,2	2,80-2,83	2,74-2,78	2,72-2,75	200-350	4,0-4,5	1,8-2,0	0,85-1,00
	2,9	2,82	2,76	2,74	260	4,2	1,9	0,95
XIX (XXIV)	1,2-1,7	2,75-2,80	2,73-2,77	2,71-2,75	6 000-10 000	5,6-5,9	0,3-0,9	0,05-0,35
	1,4	2,78	2,75	2,74	7 000	5,8	0,5	0,15
XX (XXV)	1,5-2,0	2,78-2,84	2,75-2,80	2,73-2,79	1 500-7 000	5,4-5,8	0,6-1,2	0,20-0,55
	1,8	2,81	2,78	2,76	3 700	5,6	0,9	0,35

XXI (XXVI)	$\frac{1,8-2,3}{2,0}$	$\frac{2,80-2,87}{2,84}$	$\frac{2,77-2,83}{2,80}$	$\frac{2,76-2,80}{2,78}$	$\frac{700-300}{1100}$	$\frac{5,2-5,7}{5,4}$	$\frac{0,9-1,5}{1,2}$	$\frac{0,35-0,70}{0,55}$
XXII (XXVII)	$\frac{2,0-2,5}{2,2}$	$\frac{2,84-2,88}{2,87}$	$\frac{2,79-2,85}{2,83}$	$\frac{2,78-2,83}{2,81}$	$\frac{500-1500}{700}$	$\frac{5,0-5,5}{5,3}$	$\frac{1,1-1,6}{1,3}$	$\frac{0,50-0,75}{0,60}$
XXIII (XXVIII)	$\frac{1,3-1,9}{1,5}$	$\frac{2,74-2,82}{2,76}$	$\frac{2,73-2,79}{2,74}$	$\frac{2,73-2,78}{2,72}$	$\frac{2000-10000}{7000}$	$\frac{5,5-6,0}{5,8}$	$\frac{0,2-1,1}{0,6}$	$\frac{0-0,50}{0,20}$

Note. Numerator: value ranges; denominator: average values.

TABLE 4. Petrophysical and Compositional Characteristics of Coals and Coal-Bearing Rocks in Part of Mine No. 1

Petrophysical type		Compositional characteristics						Petrographic characteristics		
No.	designation	organic matter	mineral matter	mineral admixtures				color	luster	textural structure
				clay matter	sulfides	carbonate matter	clastic matter			
XXIX	Shale, clayey, low carbon content	10-20	80-90	60-90	0-5	0-15	0-20	Dark gray, black	matte	Banded layered
XXX	Shale, clayey, medium carbon content	20-35	65-80	55-80	0-5	0-10	0-10	Same	"	Uniform, striated, banded
XXXI	Shale, clayey, high carbon content	35-50	50-65	50-65	0-5	0-7	0-7	"	Semimat, matte	Banded, striated
XXXII	Anthracite, high ash content	50-70	30-50	30-50	0-5	0-5	0-5	matte	Semimat	Microbanded
XXXIII	Anthracite, medium ash content	70-85	15-30	15-30	0-5	0-3	0-3	"	Semilustrous	
XXXIV	Anthracite, low ash content	85-100	0-15	0-15	0-5	0-1	0-1	Grayish black, with yellow hue	Lustrous	Uniform, faintly banded

of elastic longitudinal waves decreases from 3400-4100 m/sec (in clayey shales with low and intermediate coal content), to 2600-2900 m/sec (low and medium ash anthracites). The intensity of natural gamma radiation increases from 0.2-0.6 pA/kg (anthracites) to 1.5-1.7 pA/kg (clayey, medium- and low-carbonaceous shales).

The chemical composition of rocks displayed a gradual change between various categories. In carbonate-free rocks the following changes occurred at the lithofacies transition from coarse sandstones to medium and fine-grained sandstones, and toward aleurolitic-clayey and clayey shales: the Al-oxide content increased from 3 to 21%, bivalent iron from 1.5 to 7.2%, Mg from 0.3 to 3.7%, K from 0.8 to 3.4%, Ti from 0.15 to 0.9%; the Si content dropped from 88% to 50%. At the transition from clayey shales and sandstones with clayey cement, toward rocks with carbonate cement, a steady increase in Ca-oxides occurs (from 2 to 13%). The Mg-oxides increase from 0.3 to 4.9%, CO₂ from 1 to 16% and the other oxides decrease (Fig. 3). Limestones and carbonate rocks contain the highest Ca-oxide concentrations (24-44%), CO₂ (29-38%), Mg (2.7-7.5%), bivalent iron (5.5-7.5). They contain minimum amounts of Si-oxides (10-28%) and Al-oxides (2-10%), in comparison with other rocks. The Ti, P, Mn, and S-oxide content remained below 1% in all petrophysical categories (Fig. 3).

This classification provides a sevenfold increase in the details through the use of composition data, as compared with geology and geophysics methods. The lithotype concept also utilizes petrophysical indices. These (the record of eight lithological-geophysical stages, observe in anthracite-bearing Donets Basin deposits) resulted in $34 \times 8 = 272$ lithotypes in coal-bearing units with anthracite coals.

Thirty-four petrophysical types of rocks and coals were identified in coal-bearing rocks in analogous lithological-geophysical classifications for other lithological-geophysical stages with units that include anthracite coal. These had been defined only on the basis of different physical parameters, caused by epigenetic changes in the deposits.

Based on the GIS method, the geological-geophysical classification thus allows the subdivision of a given section into component beds, to identify their thickness, structure, deposition depth, petrographic rock types and their clayey, clastic, carbonate and organic components, as well as their chemical makeup [2, 6].

PETROPHYSICAL CROSS SECTION OF COAL-BEARING BEDS WITH ANTHRACITE

COALS

Geological-geophysical studies led to construction of a composite petrophysical section, representing all Donets Basin units that contain anthracite coals (Fig. 7). The section, 4000 m thick, include all metagenetic deposits in the Donets Basin between stages XIII (PA₁) and XIX (A₃). It was constructed by gradual combination of individual anthracite-bearing petrophysical sections in the studied region, with data on petrophysical changes and altered characteristics of anthracites (mineral density of organic mass, volume of exiting volatiles and logarithm of electric resistivity).

The section displayed the thickness of deposits in the metagenetic stage in the rocks, and also the depth of greatest rock burial during the period of progressive epigenesis. These were determined by the composite petrophysical Donets Basin section [2, 4]. The petrophysical section illustrates the quantitative changes in physical characteristics (K_p , δ_M , δ_N , δ_S , ρ_p , I_y) in each petrophysical category throughout the entire section of coal-bearing units with anthracite coals. The changes during the period of progressive epigenesis occurred at different burial depths, influencing the physical characteristics that the coals and rocks attained at given PT-conditions [2, 4].

The porosity (K_p) of all petrophysical types displays a relatively narrow range of values (between 1-3 volume percentages). Porosity differences of most lithotypes fall within the range of error in K_p -determination. These differences were identified and followed only due to massive changes in K_p , through simultaneous microscopic petrographic studies of each investigated samples and by the subsequent correlation of the results.

In the upper part of the section, the porosity of many clayey and detrital rocks is identical and has maximum values, in comparison with all the other lithotypes. Maximum K_p values characterize the carbonate rocks (types XIX-XXIII) and limestones (XXIV-XXVIII) there. Intermediate K_p values occurred in rocks with 10-50% carbonate content (types VII, X, XII, XIV, XVI, and XVII).

The porosity values show contrasts between the various lithotypes in the lower part of the section. It results from the uneven changes in K_p values in various lithotypes throughout the section. The greatest (0.2-0.5% of total volume) gradient values of K_p (change per 1000 m of the section) occurred in coarse-, medium and fine-grained sandstones with clayey cement and aleurolitic shales (types I, III, VI, IX, XII), with minimal (0.01-0.16 vol.%) in limestones (type XXIV-XXVIII), carbonate rocks (types XIX-XXII) and clayey shales (type XXVIII). This causes inversion of the K_p values in these lithotypes in metagenetic stages XV-XIX (Fig. 7).

The mineral density (δ_M) of coal-bearing rocks increases downward in the section from 2680-2860 to 2690-2890 kg/m³. These changes in clayey rocks occurred through recrystallization of illite and chlorite into secondary sericite and muscovite; in clastic rocks, through formation of quartz cement in the form of secondary (regenerated) quartz; in carbonate rocks and limestones, through dolomitization. These processes show that the rocks' δ_M values developed at gradients of 3-11 kg/m³ per 1000 m of section. Secondary mineralization in clastic rocks occurred with lesser intensity, in comparison with other lithotypes. In these rocks the δ_M -increase had the least gradient (3-6 kg/m³). Aleurolitic-clayey and clayey shales (types XV, XVI, and XIII) had maximum gradients (8-11 kg/m³). Various δ_M -values were caused by inversion of the δ_M values in certain lithotypes in metagenetic stages XIII-XV (Fig. 7).

The combined effects of the two rock alteration processes with increasing PT-conditions results in gravitational density increase and recrystallization that lead to decreasing porosity and increase in mineral density in each lithotype of the section. The volume density increases, as the result (in the δ_N of water-saturated rocks and the δ_S -values of completely dry rocks). Specific electric resistance values (ρ_p) and the propagation speed of longitudinal elastic waves (v_p) also increase.

Increase in the δ_N values of rocks along the section displayed a minimum of 2630-2820 kg/m³ (in the upper part of the section; stage XIX) and a maximum of 2670-2840 kg/m³ (in the lower part of the section; stage XIX). Changes in the δ_N -values of various lithotypes occurred along uneven gradients; from 3-6 kg/m³ (limestones and carbonate rocks) to 8-14 kg/m³ per 1000 m of section (in sandstones, clayey shales and mixed clayey-carbonate rocks). Due to these varying gradients the δ_N -values displayed inversion in certain lithotypes (Fig. 7).

Changes in the δ_S values in the reviewed metagenetic stages were similar to that of δ_N , but were of somewhat higher gradients (by 3-5 kg/m³). Inversion of the δ_S -values also occurs in certain lithotypes (Fig. 7).

The ρ_p values of the lithotypes increase from 180-5600 (in the upper section) to 260-8200 $\Omega \cdot m$ (in the lower parts). Due to the great impact of pore water mineralization and of the temperature on the ρ_p -values with other conditions being equal, this parameter was conditionally established, assuming uniform pore water mineralization ($C = 0.6$ g/liter) and temperature ($T = 20^\circ C$).

Increase in the ρ_p -values is characterized by various gradients per 1000 m sections: from 20-30 $\Omega \cdot m$ (clayey shales), to 200-700 $\Omega \cdot m$ (sandstones). High ρ_p gradients in the sandstones were due to cementation of water-transmitting, small-diameter conduits and interruption in electric connections, due to formation of secondary quartz under uniform conditions of lower porosity. In clayey rocks reduced porosity and recrystallization of illite also lead to higher values of ρ_p . This increase, however, is less significant than in sandstones, due to the surficial conductance of clay minerals that did not disappear from these rocks during ep- and metagenetic alterations. Inversion of the ρ_p -values in the lithotypes was not noted in the anthracite-bearing deposits.

The v_p values of the rocks increase from 4000-5600 (in the upper section) to 4300-5800 m/sec (in the lower part). The minimum gradient (40-50 m/sec/per 1000 m section) of these values were found in limestones and clayey shales; the maximum values (80-110 m/sec) in sandstones. In these lithotypes of the lower part of the section (stage XIX) the v_p values were inverted (Fig. 7).

The intensity of natural gamma radiation (I_γ) in coal-bearing rock did not much change during metagenetic alteration. The ⁴⁰K-ion concentration in clay minerals, responsible for the rock radioactivity did not change during density increase and recrystallization. This explains the constancy of I_γ -values in each lithotype in the discussed section. All lithotypes of the coal-bearing rocks displayed 0.2-2.0 pA/kg I_γ values (Fig. 7).

Stage	Index	Number	N _{max} , km	h _c , km	Lithologic grade	K _p , %				δ _M , 10 ⁻⁴ kg/m ³			δ _N , 10 ⁻⁴ kg/m ³			δ _M , 10 ⁻⁴ kg/m ³			ρ _p , Ω·m	v _p , 10 ⁻³ kg/n			ρ _A , 10 ⁻⁴ kg			rel. units			
						1	2	3	4	2,70	2,50	2,30	2,70	2,70	2,50	2,60	2,70	2,80		4,00	80,10	4,0	5,0	6,0	0,7	1,0	2,0	0,7	1,0
XII	T ₂		0,6	0,5		13,28	18	15	4,6	22,27	1	22,27	1	22,27	1	22,27	1	22,27	1	10,11	12	10	11,15	1,24	1,24	11	1,24	1,24	11
XIII	PA ₁		6,5	0,5	1	13,28	18	15	4,6	22,27	1	22,27	1	22,27	1	22,27	1	22,27	1	10,11	12	10	11,15	1,24	1,24	11	1,24	1,24	11
		2			14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24
XIV	PA ₂		7,0	0,5	3	14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24	1,24
		4			14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24
XV	A ₁		7,5	0,5	4	14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24	1,24
		5			14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24
XVI	A ₂		8,0	0,5	5	14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24	1,24
		6			14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24
XVII	A ₃		8,65	0,05	6	14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24	1,24
		7			14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24
XVIII	A ₄		9,4	0,15	7	14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24	1,24
		8			14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24
XIX	A ₅		10,0	0,6	8	14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24	1,24
		9			14,13	15	3,6	21,26	13	26	13	26	13	26	13	26	13	26	13	26	13	11,22	15	10,21	2,3	2,3	1,24	1,24	1,24

Fig. 7. Composite petrophysical diagram of coal-bearing rocks in the anthracite deposits of the Donets Basin. Petrophysical rock types, their designation given in Table 2; physical rock characteristics; Table 3.

A very uneven frequency distribution was established for the lithotypes (Table 2). Based on thickness values, the most common lithotypes were clayey-aleurolitic shales (44%), Next came aleurolitic-clayey shales (16%), close-grained sandstone and argillaceous cement (12%), clayey shales (10%) and medium-grained sandstones with clayey cement (4%). Limestones and carbonate rocks with 50-70% carbonate content displayed minimum (0.1-0.2%) frequency. The other lithotypes occupied intermediate frequency position in the section between the noted ones.

The frequency distribution of lithotypes in the section, based on layers 5 cm and thicker, primarily depended on the ratio of these lithotypes in the total thickness of the sequence with the exception of fine-grained sandstones with clayey cement, clayey-aleurolitic and aleurolitic-clayey shales for which a wide difference exists between their thickness frequency and the number of layers (Table 2).

The established petrophysical patterns of anthracitic coal-bearing deposits, according to data from the studied regions and lithological-geophysical stages (Table 1, Figs. 1 and 7) occur throughout all the remaining Donets Basin anthracite deposits for the following reasons. First, composition of the lithotypes was determined by the component ratio (of clastic, clayey, carbonate, coaly matter components and the granulometric fractions), irrespective of the source area. Second, the physical characteristics of the lithotypes are determined by the ancient PT-conditions and not by the present location of the deposits. As the earlier PT-conditions of specific alteration stages and grades of the anthracite deposits were identical and a given lithotype represents a specific combination of petrographic components, these physical features of the identified specific lithotypes remain essentially identical throughout the entire Donets Basin area within the coal-bearing sequence that includes anthracite coals. This also holds true for the value of specific electric resistance if the ground water mineral content and rock temperature is equal between the various regions. As this does not happen, when correlation and drawing generalizations, one should utilize the different values of ρ_p , along with standard values for mineral content and temperature. In all of our studies we have employed a standard value for mineral content in ground water (0.6 g/liter) and for temperature (20°C). The other studied rock parameters are not significantly influenced by the mineral content of pore waters.

The principle of uniformity of physical characteristics in coal-bearing deposits [2] also confirms our conclusions.

It is emphasized that with uniform physical characteristics of specific lithotypes in given lithological-geophysical stages the relative distribution pattern of the lithotypes in the section may change from place-to-place. This is shown by the lithological and lithological-stability sections of the topmost parts and overlying soils of the coal beds and indicates the need to study such intervals in detail in each exploration drillhole.

Thus, the geological-geophysical method, by the use of highly efficient GIS methods in all coal-exploration drillhole sections allows a complete and reliable, detailed study of the lithology of coal-bearing deposits. In doing so, it provides a high degree of reliability in the solution of many geological tasks that are based on lithological data.

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FACIES AND GENETIC ANALYSIS OF EARLY GEOSYNCLINAL PREFLYSCH COMPLEXES OF THE NORTHERN TIEN SHAN CALEDONIDES

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The results of facies and genetic analysis are reported which has been undertaken for the first time in a study of the preflysch stage of development of the Tien Shan Caledonide geosyncline. Based on new faunistic finds the ages of the suites have been revised, and the vertical sequence of the suites previously accepted has been unfolded into a lateral series.

Ample data on the geology of the seafloor in Recent oceans and marginal seas collected in the past few years, in particular on volcanism and sedimentary processes [1, 2, 21, etc.], have enabled geologists to compare these data and determine common features with early geosynclinal formations of young and ancient folded belts. A series of monographs by lithologists from the Geological Institute of the USSR Academy of Sciences [4, 20, 23] and a number of articles on studies of individual indicator formations belong to this group.

While realizing that a complete analogy is not justified, the authors rely on information on Recent sedimentation in oceans and marginal seas as a basis for reconstructing the sedimentary processes and volcanism in the geosynclinal basins of the geological past. Volcanogenic formations, which are indicators of the tectonic regime, are especially informative. By studying their petrochemical characteristics and their position in the profile, one can determine with some certainty the type of crust of geosynclinal basins at the early stages in their history. However, they cannot characterize the type of sedimentation basis, its morphometry, and the paleogeographic settings of sediment accumulation. For these purposes the data of studies of sedimentary and volcanogenic-sedimentary complexes occurring in association with volcanic formations have been utilized with increasing success.

The paleogeographic aspect of lithologic studies of ancient strata offers a broad opportunity for interpreting these beds actualistically, since the past sedimentogenesis processes can be analyzed in detail in the present conditions.

The potential of the actualistic method was appreciated after studies of seafloor sediments of Recent basins were extended to the facies and genesis of these sediments [14, 19, 24, 25, 32, etc.].

For ancient formations, correlations of facies and genetic types of sediments are only possible if the correlations of profiles are reliable; much attention is therefore paid to the stratigraphy of these beds.

By differences in the upper Precambrian and Lower Paleozoic, the northern Tien Shan is subdivided into Talas-Karatau and Kirghiz-Terskei structural-formational zones. The early Paleozoic sedimentation history of Talas-Karatau zone was determined by the accumulation of uniform carbonate formations. The lower portion of the transgressive carbonate series consists of thin Vendian autochthonous terrigenous-carbonate and a Lower Cambrian (Tommotian) phosphorite-bearing silicic-carbonate formations.

The stratigraphy of the Lower Paleozoic Tamda series of the Talas-Karatau zone has been described in detail. All the series of the Cambrian system and the Lower and Middle Ordovician have been identified by various groups of faunistic remains.

In the Kirghiz-Terskei zone of Tien Shan in the Early Paleozoic, multifacies formations accumulated: volcanogenic, volcanogenic-terrigenous, and terrigenous. The stratigraphic scheme of these deposits has been worked out starting from Arenigian on the basis of graptolites [7]. This age interval is the time of accumulation of the flysch and flysch-molasse

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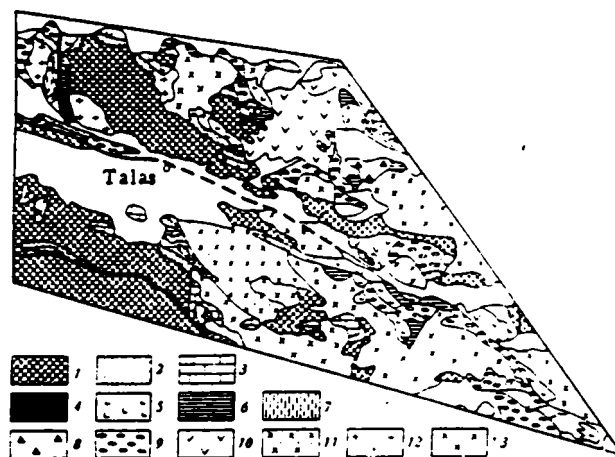


Fig. 1. Distribution of Early Caledonide facies-genetic complexes of the western Kirghiz Tien Shan: 1) protrusions of Precambrian sialic basement; 2) continental and epicontinental-sea graben facies (R_3 -V); (3-8) rock complexes $\epsilon + O_1$; 3) shelf carbonate; 4) melanocratic basement protrusions; 5) volcanic rises (tholeiitic basalts of oceanic and andesite basalts of island arc type); 6) hemipelagic sediments of deep-sea basins; 7) turbidites and fluxoturbidites of the foot of the continental slope; 8) pyroclastic flows and tephroturbidites of the foot of volcanic rises; 9) flysch and flysch-molasse sets of residual deep-sea basins O_2 ; 10) volcanogenic-molasse complexes of epicontinental basins D_1 ; 11) Late Riphean granitoids; 12) Early Ordovician granodiorites and quartz monzonites; 13) Late Ordovician and Silurian granites.

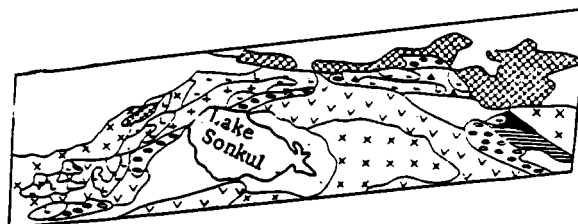


Fig. 2. Distribution of Early Caledonide facies-genetic complexes of the Sonkul area of Tien Shan. Notations as in Fig. 1.

formation of this zone. The accumulation time of the preflysch formations had been estimated nominally or from rare single finds of trilobites, brachiopods, or graptolites. The Lower Paleozoic sedimentary column of the preflysch stage was constructed as the following bottom-to-top series: Karakatty suite of basic effusives (ϵ_1 ?), Karadzhorgo tuffogenic-argillite-silicic suite with limestones (ϵ_2 - O_1), sandstone, siltstone (O_1) (Tuyuksai and Kurusai suites and their analogs), sandstone, conglomerate, and tuffosandstones with lenses of limestones of the Keptash suite (O_{1-2}). Normal stratigraphic relationships of these subdivisions are not observed anywhere. The massive recent effort to prepare memoranda for maps of the scale 1:50,000 resulted in new finds of faunistic (mainly microfaunistic) remains in the Lower Paleozoic strata. These include finds of radiolaria, sponge spicules, algae, phyto- and zoo-species, conodonts, gastropods, and ostracods [11, 18, 26]. The new data resulted in a revision of the age of these suites, so that the vertical thickness adopted previously was converted into a lateral series. The Karakatty, Kotudzha, and "Lower Ordovician" (sandstone and shale) suites can be currently dated as $\epsilon + O_1$. Detailed paleontologic and stratigraphic work will be required to prepare local stratigraphic schemes of these strata and correlate them to the general scale.

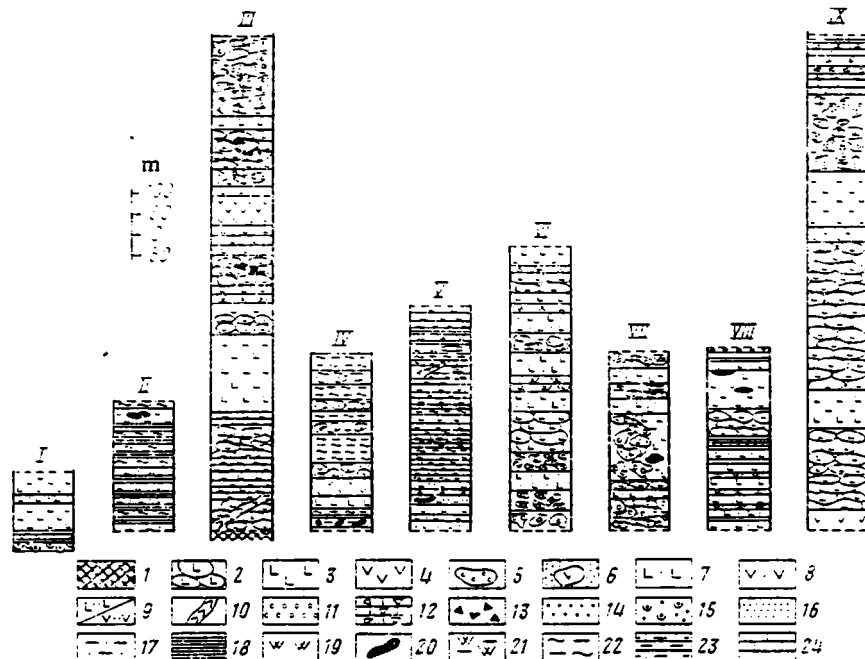


Fig. 3. Profiles of the formation of tholeiitic basalts and andesitic basalts of the Western Kirghiz ridge (I-VI), Susamyr ridge (VII), and Karakatty ridge (VIII-IX): (I) Tersk suite along the Kara-Archa River; (II) Kichi-Kainda suite along the Kara-Archa River; (III) Kara-Archa suite along the Kara-Archa River; (IV) Aibolcha shite on the water shed of Sugaty-Kichi-Kaindy Rivers (after Makarov and Razboinikov); (V) Terek suite along the Kurgantash River; (VI) Terek suite along Terek River; (VII) Kara-Archa suite along the Arams River; (VIII) Karakatty suite along the Karakatty River (northern slope); (IX) Karakatty suite along the southern slope of the ridge. (1) melanocratic basement; (2) amygdaloidal basaltic porphyrites with pillow separates; (3) basaltic porphyrites, spilites, hyalobasalts; (4) andesite porphyrites; (5) clastic lavas; (6) agglomeratic tuff of andesitic porphyrite; (7) tuff (psammitic, psephitic, agglomerate); (8) tuff of andesitic porphyrites; (9) tuffites; (10) gabbro diabase and diabase dikes; (11) conglomerate; (12) (mainly carbonate) olistotromes; (13) edaphogenic breccias, mainly silicic; (14) gritstone; (15) quartzite; (16) sandstone; (17) siltstone; (18) argillite (phyllite); (19) flint; (20) jasper; (21) flint-shale interstratification; (22) clay-silicic shales; (23) limestone in alternation with siltstone; (24) limestone.

Stratigraphic investigations were accompanied by lithologic and formational analysis of the sediments of the preflysch stage in the development of the Caledonian eugeosynclinal region. A classification of the sets of rocks has been prepared and used as a basis for reconstructing the sedimentation regimes of the Early Paleozoic sedimentation basin, its morphometry, and its evolution.

Several formations were identified in this stage: tholeiitic basalts and andesite basalts, hemipelagic terrigenous-silicic-tuff formation, terrigenous formations with cherts of the foot of the continental slope, and effusive-silicic-tuff-terrigenous formations of the foot of volcanic structures. Within the Talas-Karatsu structural formation zone, situated to the south, a thick carbonate formation accumulated during the Early Paleozoic, which was characteristic of a shelf sedimentation environment. It is not considered in this paper. The location of these units in the western and central Northern Tien Shan is illustrated by Figs. 1 and 2.

The rocks constituting these formations are grouped as a series of paragenetic rock complexes (associations); their spatial occurrence characterizes the primary facies zonality

of the sedimentation basin. Each facies unit is characterized by a predominant development of some single rock complex (association), which does not rule out the presence of fragments of other rock associations as secondary units, especially in areas where different facies were adjacent to each other.

The complex of tholeiitic basalts and andesite basalts forms the core of the formation named after this set of rocks and in volume corresponds to the Karakatty suite and its stratigraphic analogs: Kara-Archa and Terek suites (Fig. 3). The age of the Karakatty suite has been determined provisionally as Early Cambrian, based on single finds of sponge spicules and radiolaria. Numerous algae, acritarchs, conodonts, etc., have been found recently in the rocks of this suite, expanding the age range of the suite from O_1 to O_1 , inclusive [17, 18]. It is possible that the lower age boundary could be in the Vendian.

The outcrops of the Lower Paleozoic volcanogenic series are usually limited to faults. In the belt of exposures of the Lower Paleozoic ophiolites, whose narrow suture has been preserved at the juncture of northern and middle Tien Shan [15], the volcanogenic suite occurs on a melanocratic basement (see Fig. 3, III). The relationships of these rocks are often disrupted by faults; in some areas (Kavak-Tau and Karadzhorgo ridges) a normal occurrence of basalts on the basement has been preserved. For all exposures of melanocratic basement a prevalence of striated taxitic metasomatic gabbroids and amphibolites with relicts of ultrabasites is typical.

In allochthonous slices within the Makbal-Burkhan Baikalin geanticlinal zone, the base of the volcanogenic series is composed of a formation of quartzose and arkosic sandstones (Ovsk-Dzhel'dysui suite). Its constituent rocks are decay products of the ancient folded granitized basement (see Fig. 3, I).

An oblique stratification in the sandstones and the presence of glauconite are signs of shallow-sea environments. The thickness of the Ovsk suite ranges from 70 to 450 m. The suite occurs transgressively on various subjacent sediments and includes a crust of weathering developed on these sediments at the base of the suite.

In the Talas-Karatau zone, graben formations developed before the Lower Paleozoic limestone-dolomitic shelf sediments. In the lower portion of the zone the grabens are represented by a terrigenous arkosic formation which occurs disconformally, sometimes with angular disconformity on Upper Riphean sediments. Terrigenous arkosic formation is succeeded up the section by tuff carbonate-argillite-silicic and terrigenous-pyroclastic formations, which are combined to form the Malokaroi Vendian series [16]. Its thickness is 1000-1500 m on average. Generally, this orogenic complex is characterized by obliquely stratified coarse-grained molassoid sediments, which are often red, and include volcanogenic, mainly explosive rocks of trachyliparite and dacite series at their tops [8, 19]. The profile of the graben facies of the Talas-Karatau zone is crowned by tilloid rocks of the Konyrtyube suite (70-100 m). In the middle Tien Shan the Vendian volcanogenic-molassic sediments occur on a thick (up to 3000 m) sparagmitic group of formations.

The petrography and petrochemistry of the volcanites the Karakatty suite are relatively well studied [6, 10, 17]. The volcanic series proper is divided into two parts by composition. The lower part is made up mainly of massive amygdaloidal basaltic porphyrites and spilites; diabases and trachybasalts are less common and confined to the upper part of the formation bottom.

The upper portion of the volcanogenic series (the andesite-basalt part) exhibits a diversity of the composition of volcanic rocks and their textures. They appear as covers rapidly wedging out and lava streams of a variable thickness, often with spherical and pillow isolates. These are separated by horizons of pyroclastics. The balance of the effusive and explosive material is on the whole retained, but in different parts of the northern Tien Shan their proportions vary in a broad range (see Fig. 3, III-IX). The bulk of this part of the volcanogenic series consists of basaltic porphyrites and andesite basalts. Less common are spilites, variolites, trachybasalts, trachyandesites, jasper, and flint. Petrochemical studies of volcanites have indicated a pronounced predominance of basalts of high-alumina and tholeiitic series [6, 12].

The effusives at the top of the series are better differentiated by silicic acid. Along with the mode in the basalt region, differentiates up to the andesite are present with the direction of the differentiation following the calcareous-alkaline trend. At the top of the series trachybasalts and trachyandesites, dikes, and orthophyric sills appear.

Mineral parageneses, textures, and composition of volcanites provide some indications on the type of magmatic sources and effusions and the geodynamic settings in which they were formed.

Volcanic effusions were submarine, as confirmed by the widespread pillow lava. Amygdaloidal textures and frequent spinifex textures are evidence of gas saturation of the lava and a shallow depth of effusions.

In extensive zones, volcanic activity probably occurred as crack effusions similar to what is observed in Iceland at present [31]. Thick coarse pyroclastic streams and the abundant tuffs in the profiles of the volcanogenic strata of some areas (Keptash trough) that were spread over large distances and penetrated into neighboring deep-sea depressions where rhythmic rocks were formed, make the eruptions in these areas similar Peleian type.

The sedimentary and volcanogenic-sedimentary complexes enclosed in the volcanogenic complex are closely related with the beds denoted by the common name of Karadzhorgo suite and widespread in northern Tien Shan.

A characteristic trait of this suite, by which it can be recognized, is the variegated bright-cherry and green pigmentation of thinly striated clay, silicic, and silt schists, which sometimes contain chert interlayers, as well as the presence of limestone blocks in sandstones and conglomerates.

The suite displays considerable lateral variations. The volume of the rocks in the suite thus varies from region to region: in the western part of the Kirghiz ridge it is mainly volcanogenic; in the Susamyr ridge, volcanogenic-clastic; in Dzhumgal ridge, volcanogenic-terrigenous; in Karadzhorgo ridge, terrigenous, etc. Even within a single location the profiles of this suite may differ noticeably in the blocks.

Numerous collections of trilobites date the formation of the suite as a period between the Early Amga age of the Middle Cambrian through the Tremadocian [22]. At the top of the suite, in Kungei Ala-Too ridge, Zima discovered Early Tremadocian graptolites. At the bottom of the carbonate olistoplaque, in Kastek ridge, Vologdin collected and identified epiphytons, poorly preserved archeocyathids, and sponges of the Lower Cambrian. In the terrigenous-carbonate strata surrounding it, remains of the Middle and Upper Cambrian brachiopods (determinations by Goryanskii) and Upper Cambrian trilobites (determinations of Goncharova) have been collected. The recent finds of conodonts, chylolites, and other microfaunistic remains confirm this age of the suite. The Karadzhorgo suite has tectonic correlations with the volcanogenic Karakatty suite in virtually all areas where it appears; it is closely connected with the latter by abundant volcanic and volcanogenic clastic material. These correlations, however, are not temporal but spatial, as indicated by faunistic finds in the Karakatty suite.

Khrstov and Chernyshuk [26] discovered in the Dzhumgal ridge an occurrence of Karadzhorgo suite upon Proterozoic crystalline schists, whose fragments are found in basal horizons of the suite. In a different block, the Karadzhorgo suite apparently occurs on gabbro-amphibolites. The latter have been found in the mélange zones as blocks where direct contact has been traced.

The Karadzhorgo suite is overlain with an erosion by Arenigian conglomerates and sandstones that open a thick flysch bed.

The rocks of the suite are grouped by composition and structure into several major complexes: hemipelagic variegated argillite-siltstone-silicic complex, the complex of terrigenous and volcanoclastic turbidites and fluxoturbidites, and the olistostromic complex.

The complex of hemipelagic variegated argillite-siltstone-silicic shales. The main components of this complex are red and greenish clay-silicic silt-clay schists of a lumpy texture and finely striated structure, heavily pigmented with iron hydroxides and inclusions of small psammitic fragments (1-3%) of plagioclase, quartz, and mica flakes. Sponge spicules abound. The schists contain interlayers (numerous in some profiles) of siltstones, fine-grained sandstones, and tephroids, from 1 to 10 cm thick. Layers of 2.5-3 cm are typical. They have distinct contacts with schists and are of a horizontally stratified, sometimes lens-shaped habitus (Fig. 4b, c). Unidirectional oblique layering is observed sometimes. Most of these sandstones have no regular internal organization. Direct and inverse gradational stratification is sometimes observed: small-grained sandstone-siltstone-argillite. Deformation and ooze slump structures are seen in rare horizons. The textural and structural features of the sandstones allowed classifying them as contourites [30]. There are no wave surf signs on layering

surfaces, but current ripples are sometimes observed. Intrusion features are present. Carbonate matter is practically absent in the shales. The maximum thickness of the argillite-siltstone-silicic shale complex is 150-200 m.

The foregoing features suggest a relatively deep-sea environment (beneath the level of carbonate compensation) of the accumulation of clayey and clayey-silicic ooze. A set of thin lenses and interlayers of limestones at the top of this complex in some locations indicates a periodic rise of the sedimentation basin floor above this level. The influx of coarser silt and psammitic material was introduced by bottom currents. Similar lithologic-genetic formations have been determined in Recent sediments in the northwestern Atlantic [27] and the ancient strata of the South Urals [23].

In the depressions that were directly adjacent to volcanic structures or to the foot of the continental slopes, the hemipelagic sediments were divided by coarse outflows of terrigenous and volcanogenic-terrigenous turbidites and fluxoturbidites, which at times superseded hemipelagic sediments (Fig. 5).

Silicic rocks (silicites) usually associate with clay-silicic and clayey shales. They form layers and lenses, from a few centimeters to 20 m thick, made up of plate-shaped varieties. Mostly they are green, less often gray or black. The texture is cryptocrystalline. The flints often contain an admixture of pyroclastic or clay material. Radiolaria and sponge spicules are frequent. Silicites form a continuous series through clay silicites to argillites.

The complex of fluxoturbites and turbidites is represented by sandstones: graywacke and polymictic, from small- to coarse-grained, siltstones, argillites, gritstones, conglomerates, and tuffs. Most of the sandstones and gritstones of Karadzhorgo suite exhibit horizontal stratification and no oblique stratification. Layers vary in thickness from 0.5 to 3 m. The sorting of clastic material in the gradational layers is observed in only some of the horizons; pendular stratification is more common. In that case, gravel fragments are found in the middle of the sandstone layers.

The sandstones are typically coarse-grained, less often medium-grained. The contents of the clay component is low. An uneven granularity of clastic material is characteristic. Portions with coarser-grained gravel material can be found at all levels of the sandstone layer. Sandstones also often include "floating" fragments of clay, clay-silicic, and silicic, sometimes striated, shales. The fragments are of an angular unrounded shape, with rounded varieties found infrequently. The fragments are sometimes oriented in conformity with the bedding (see Fig. 4a, f). The degree of saturation of sandstones with such floating fragments varies broadly: from rare finds to abundance. On the layering surfaces of sandstones no signs of currents or ripples are seen; only load molds can be observed.

The textural and structural features of sandstones allow classifying them as autokinetic grain flow sediments. These sediments were denoted by the term fluxoturbidites in [29]. Voznesenskaya [4] suggested the term grainites. Fluxoturbidites in the Karadzhorgo suite occur in a close association with turbidites.

Turbidites are distinguished from the coarser unsorted fluxoturbidites by their better-sorted gradational stratification and the presence of silt and argillite rock varieties. They form multilayers 2.5-3.5 m thick. Generally, for turbidite multilayer, the prevalent granulometric sizes are observed to decrease from the bottom to the top of the layers. A complete profile of a turbidite described by Bouma [28] can be observed in few multilayers.

The fullest turbidite profile of the Karadzhorgo suite consists of the following elements of a rhythm:

A — basal sandstone with inclusions of gravel and pebbles with direct gradational stratification;

B — sandstone with horizontal stratification produced by alternating interlayers of sandstone and silty sandstone;

C — sandstone with clay matter; deformation and landslide structures and thin oblique stratification are observed; and

D — argillite or siltstone with a thin horizontal stratification.

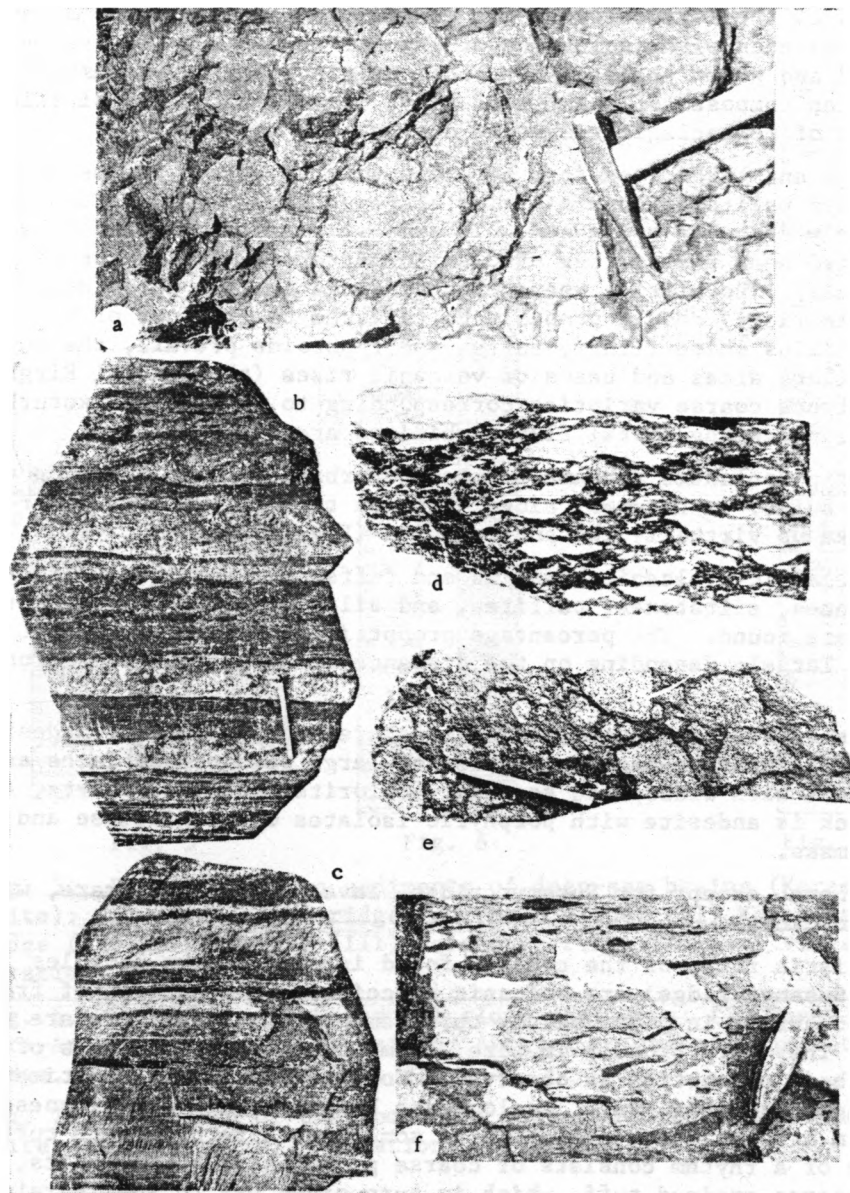


Fig. 4. Susamyr ridge, Karadzhorgo suite: (a) pyroclastic stream; (b, c) alternation of fine-grained tephroid (contourite) and red clay-silicic argillite with sponge spicules (dark interlayers); (d, e) edaphogenic breccia with fragments of carbonate (d) and sandstone (e) composition; (f) grainite (fluxoturbidite) with edaphogenic inclusions of red clay-silicic schists.

The turbidites associated with fluxoturbidites are characterized by coarser grains of sandstones and the absence of upper fine-grained members of multilayers, as opposed to the turbidites associated with hemipelagic sediments. Thicknesses of from 0.2 to 0.8 m, less often up to 1.2 m, are usual in the latter.

The foot of the turbidite horizon is often uneven with erosions and breakage of underlying lithified sediments. Signs of intrusion are seen on the layering surfaces.

The composition of sandstones of fluxoturbidites, and turbidites corresponds to typical feldspar graywackes, where the bulk of clastic matter is supplied by plagioclase (up to 65%), rock fragments (up to 30%), and flakes of chlorite, quartz, and hornblende (5%). Among rock fragments most representative are andesites, porphyrites, spilites, quartz-plagioclase porphyries, diabase porphyrites, granites, acid alkaline rocks, limestones, silicic shales, and quartzites. The fragments are cemented by a silicic-chloritic-epidotic mass.

The sandstones of the Karadzhorgo suite contain lenses and layers of gritstones and small-pebble conglomerates with inclusions of angular or semirounded fragments of clay-silicic, often striated, red and green shales of a local origin. The upper members of the turbidite multilayers are often composed of packets of clay, clay-silicic, and silicic shales, suggesting a sedimentation of hemipelagic sediments during calm seasons.

Fluxoturbidites and turbidites form horizons varying from a few meters to 300 m in thickness; they occur amid pelitomorphic silicic, clayey-silicic shales, and silty argillites, i.e., amid relatively deep-sea sediments. In some profiles they fill the suite, suggesting that they accumulated near the sources of clastic matter (Kurusai suite of the western Kirghiz ridge and other areas). Localities where clastic rocks include polymictic and arkosic material (western Kirghiz ridge) should probably be referred to the foot of the continental slope (Fig. 6). In localities where flints, tuffs, and tephroids prevail, the environments correspond to near-cordillera areas and bases of volcanic rises (the central Kirghiz ridge and other regions). In all types coarse varieties corresponding to proximal fluxoturbidites and less-coarse varieties representing distal fluxoturbidites are distinguished.

The complex of pyroclastic streams and tephroturbidites also makes up a substantial volume of Karadzhorgo suite. In Dzhumgal ridge, Keptash trough, and some other areas, the rocks of this complex make up virtually the entire suite (Fig. 7).

The true pyroclastic (volcanic breccias and tuffs) and terrigenous rocks (tephroids, tephrogenic sandstones, siltstones, tuffites, and silicic rocks) are widespread. Horizons of effusive rocks are found. The percentage proportions of the constituent rocks vary in the lateral direction, largely depending on the distance of the territories from the source of pyroclastic matter.

Effusive rocks exhibit an amygdaloidal structure and predominant andesitic and basaltic composition. Typical andesite-basalts consist of large plagioclase laths and a small amount of crystallized glass with widespread secondary chlorite, calcite, quartz, and iron hydroxides: another typical rock is andesite with porphyric isolates of plagioclase and pyroxene and small crystalline groundmass.

Almost everywhere, except for Susamyr ridge, lava horizons are rare, with beds from 1 to 3.5 to 5 m in thickness.

The characteristic rocks of the complex found in some of the profiles in large amounts (Aramsu River and Susamyr ridge) are volcanic breccias. They consist of fragments of amygdaloidal effusives occurring in poor, mainly tuff cement. The fragments are angular, sometimes slightly rounded. They vary broadly in size: from psammitic to boulders of 0.6-0.8 m in diameter. Inside the beds no sorting is observed. Coarse material is sometimes confined to the bottom of the horizon (see Fig. 4a). Agglomerate horizons vary in thickness from 5 to 80 m. Horizons of 20-60 m are typical. Agglomerates sometimes alternate with tuffs in rhythms of 1.5-2 m. The base of a rhythm consists of coarse pyroclastic stream units, succeeded with a sharp contact by coarse-grained tuff, which in turn gives way to small-grained tuff with a stream stratification. The top of the rhythm consists of fine-layered silicic tuffites.

Tuffs and tephroids are, mostly, crystalloclastic and crystallitoclastic varieties of diverse granulometry. Tuffs of andesite, diabase, and less often dacite porphyrites are distinguished; they form beds of up to 2-5 m. Amid crystalloclasts, plagioclase and pyroxenes are noticeable. Plagioclase is often albitized, intensely pelitized, and sericitized. Lithoclasts are represented by chloritized glass and amygdaloidal basalts and andesites. There is usually no sorting of material within a layer. The layers have sharp contacts; the lower contacts are sometimes erosional. Where the pyroclastic streams reached into the deep portions of the basin, they alternate with green and red clay-silicic shales and silicites. These rocks have a sequence of alternation corresponding to Bouma's model, suggesting that unequally processed pyroclastic material was supplied by turbidite flows. Three-component rhythms are common, which consist of coarse- and medium-grained tuffs tephroids of a reddish-brown, greenish, and gray color, small-grained tuffs, and silicic tuffites. Sedimentation rhythms are completed by light-gray and greenish silicites. The rhythms range from 1 to 12 m in thickness, rarely up to 30 m. At the base of coarse-grained tuff and tephroid layers, angular fragments of broken subjacent clay-silicic and silicic rocks are found.

Horizons of conglomerates, gritstones, and sandstones make up part of this complex, in addition to volcanogenic clastic matter. The composition of their detrital matter is homogeneous; it consists of andesite, dike rocks, clay-silicic red and green rocks (shales), flint, and jasper. The fragments are rounded or angular.

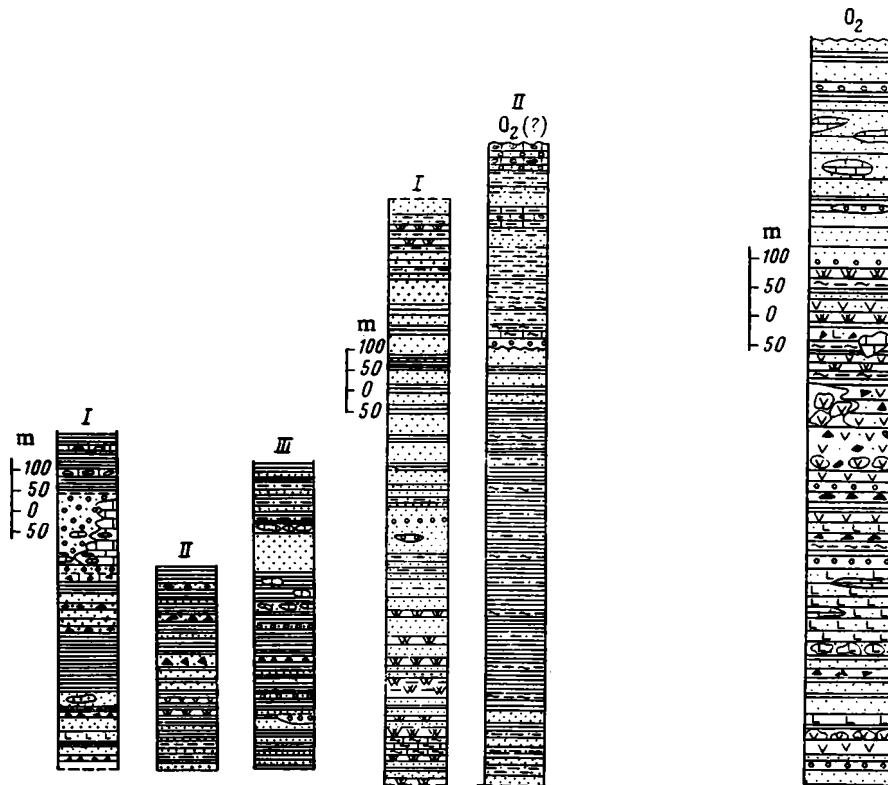


Fig. 5

Fig. 6

Fig. 7

Fig. 5. Profiles of the sediments of deep-sea basins (Karadzhorgo suite): (I) Karadzhorgo ridge (northern slope); (II) Karakatty ridge (Choloi Village); (III) Karakatty ridge (Karasai Village). Notations as in Fig. 3.

Fig. 6. Profiles of continental slope sediments: (I) Tuyuk suite, Kara-Archa River; (II) Kensai and Akterek suites of Ichkeletau ridge. Notations as in Fig. 3.

Fig. 7. Sediments of the foot of a volcanic structure (Kokkiin suite, Kirghiz ridge). Notations as in Fig. 3.

Terrigenous rock horizons contain olistoliths of various size of limestones with brachiopods (E_3-O_1).

Spasmodic influx of clastic matter consisting wholly of local rocks (effusives and cherts) is evidence of internal rises. Up the profile in Keptash trough, the number and thickness of coarse clastic horizons are seen to increase.

Clay-silicic and silicic rocks of the Karadzhorgo suite contain peculiar accumulations, classified by us as edaphogenic formations. These are usually clastic rocks (sandstone, tuffite, gritstone, breccia, and conglomerate) with angular unrounded or poorly rounded fragments of red or green clay-silicic and silicic rocks, less often limestones and sandstones. The fragments range in size from psammites to boulders. Flattened fragments are usually oriented along the course of the bed. Depending on the type of the enclosing material, several kinds of edaphogenic formations are distinguished.

Coarse-Clastic Edaphogenic Breccias. These are horizons up to 5-10 m thick consisting entirely of coarse unrounded fragments of silicic and silicic-clay rocks unloaded chaotically, totally unsorted in size, not oriented along the course of the bed, with a very small amount of and or gravel matter filling interstices between fragments (Karakatty ridge, Choloi River). Silicic-fragment edaphogenic breccias of this type are probably a result of collapse of the walls of canyon ledges.

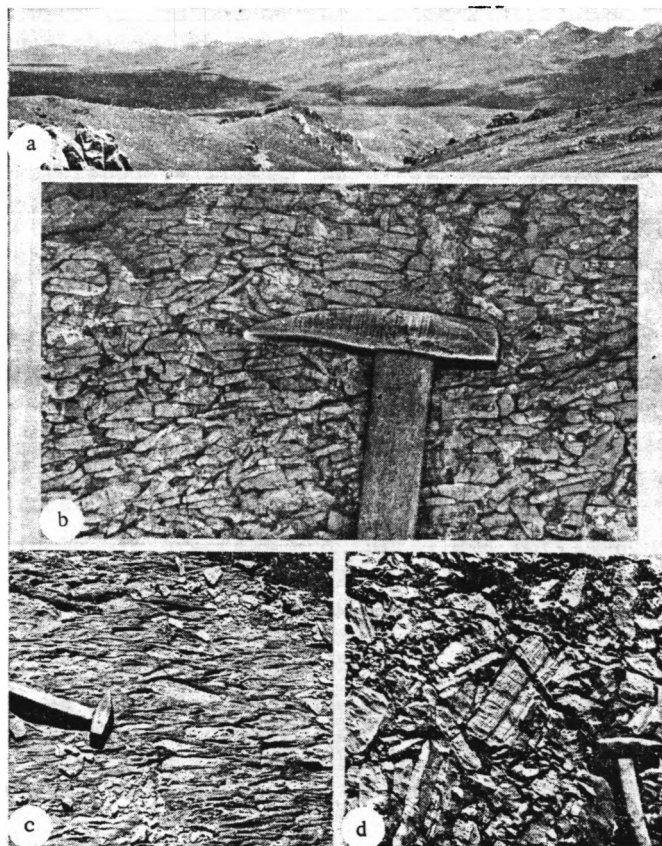


Fig. 8. Karadzhorgo ridge: (a) carbonatic olistoliths and olistoplaques in Karadzhorgo suite; (b-d) tectonic-gravitational mixtures of Karakatty olistostromes (b — tectonically disintegrated untransported material of plate limestones; c — members of alternation of limestone and clay-carbonate shales; d — tectonically disintegrated material entrained in a landslide process).

Sandstone, gritstone, tuffite, and tephroid with scattered edaphogenic fragments of cherts and clay-silicic rocks throughout the layers (see Fig. 4f) should probably be referred to deposits of grain flows which carried edaphogenic material.

The third type of rocks with edaphogenic material are turbidites. These include angular or slightly rounded fragments of silicic and clay-silicic and clay-silicic rocks in the lowermost coarse clastic layer.

The Karadzhorgo suite is unevenly saturated with horizons containing edaphogenic material. The largest number of such horizons is observed in Karakatty and Karadzhorgo ridges. The localization of edaphogenic units differs even in neighboring profiles. Grigor'ev [4] noted that the confinement of edaphogenic sedimentation to isolated local areas is typical for Phanerozoic geosynclines. It is associated with the existence of isolated ledges and cordilleras developed as a result of overthrusts and charriages (nappes).

One variety of edaphogenic breccias is olistostromes, widespread in the Karadzhorgo suite.

Many geologists have noted the presence of large exotic fragments and blocks of limestones in the Karadzhorgo suite [3]; however, they were mistaken for reefogenic formations. One of the first to identify their olistostromic nature was Ges' [5].

As has been determined recently, fragments, blocks, cliffs, and ridges of limestones are found in the development field not only of Karadzhorgo suite, but also amid Karakatty effusives, Tuyuksai sandstones, and Donor conglomerates. These units range in size from small gravels to cliffs of up to 150-200 m thick stretching from 1.5 to 6 km.

By differences of genetic features and the formation time the Lower Paleozoic olistostromes of northern Tien Shan are divided into two types according to the occurrence of their representative profiles: Karakatty and Dolon.

Karakatty olistostromes occupy a lower stratigraphic position and are composed of exposures of rootless carbonate cliffs and blocks of various size, scattered over a large area (Fig. 8a); they range in size from small lens-shaped or irregular bodies to large bodies of 100×3000 m (olistoplaques). Most of these entities are composed of pelitomorphous massive or small-crystalline marmorized light-gray and dark-gray limestone. The limestone contains an admixture of quartz and plagioclase psammitic and siltic grains which are poorly rounded or angular. Some of the lens-shaped bodies are limestone breccia and conglomerates with chaotically piled carbonate, less often other, fragments. Elongate fragments are sometimes oriented along the bed. Limestones in the fragments (olistoliths) vary in color, rounding, and secondary alteration degree. There are dark-gray, gray, brownish, pink, and striated varieties. The fragments are usually angular, but rounded forms are also found. They vary in size from 2 cm to boulders. The layers are typically saturated with such fragments. The groundmass is of a clay-carbonate composition and includes small psammitic and psephitic limestone fragments.

Large bodies (olistoplaques) are mostly massive marmorized limestones. The enclosing rocks are siltstones, argillites of a greenish or brownish color, tuffs which sometimes contain interlayers of small- and medium-grained sandstones of Karadzhorgo suite, and effusives of Karakatty suite. The carbonate bodies are in contact with them, usually on a tectonized surface. A carbonate breccia usually is the base of carbonate olistoplaque. Along with enclosing rocks, the olistoplaques are crumpled into narrow isoclinal folds and, by all features, are remains of a carbonate tectonic cover. In some areas (northern slope of Karadzhorgo ridge, Karakatty and Zailiiskii Ala-Too ridges) all transitions can be observed: from intact or slightly affected remains of the tectonic cover to olistostromal sedimentary entities. The remaining part of the cover is composed of a 200-500 m strata of massive and tabellar limestones, sometimes alternating with phyllitelike clay-carbonate schists. Layers of unshifted breccias with a typical "bamboo-leaf" texture are sometimes found amid them. These were formed after members of alternation of plate limestones (see Fig. 8b) and clay-carbonate shales with limestones (see Fig. 8a). Such layers mark the sliding surfaces of blocks of carbonate rocks flaked by horizontal movement.

The carriage-produced morphologically pronounced ledges or slopes were responsible for landslides and submarine slumps. They entrained tectonically disintegrated material of the carbonate cover (see Fig. 8d). In the landslide-slump sediments the varied material of the carbonate beds usually is already mixed. Besides carbonate and shale fragments, matter foreign to this bed appears: sandstone, chert, effusives, variegated silicic-clay shales, i.e., rocks underlying the olistostrome beds. The dilution with foreign material varies along the course.

In the southern slope of the Karakatty ridge, the olistostrome bed consists of an alternation of mixtite horizons from 2 to 20 m thick, with members of green and red sandstones, siltstones, and argillites with isolated limestone boulders, rather than consisting of uniform calcareous conglomerate breccias.

Up the profile, amid carbonate fragments and fragments of underlying rocks, pebbles alien to this locality begin to appear gradually (granite, quartzite, schist, etc.); they signal the transition to the next Dolon stage of olistostrome development.

Karakatty olistostromes thus are remains of a slightly affected or brecciated tectonic cover and submarine-slump formations scattered over all outcrop areas of the Lower Paleozoic preflysch sediments of northern Tien Shan. Leonov classified this genetic type of olistostromes as tectonic-gravitational mixtites [13].

Dolon olistostromes are found at the base of Arenigian-Llanvirnian-Llandeilian flysch. They have been previously described as Dolon conglomerates. These are proximal parts of the tails of turbidite deposits; near the northern slope of Karadzhorgo ridge they form a bed of about 150 m, composed entirely of massive greenish conglomerate. The groundmass of the conglomerate is a silt-sand rock with gravel fragment inclusions. The pebbles are usually rounded and polished. The conglomerates are mainly of a medium- and small-pebble size, but include pebbles and boulders of 5-50 cm. The boulders and large pebbles consist of green and black shaly effusives with less frequent gray and white limestone, granitoid, and jasper. The composition

of the fragments and their sizes vary strongly along the course. Within a short stretch of 5 km conglomerates become of the large-boulder type. The size of boulders reaches 1 m in diameter. They are well-rounded and saturate the rock densely. Most of the boulders and pebbles are of a granodiorite and granite composition. Limestone, sandstone effusives of a basic composition, gabbro, serpentinites, and jaspers are also present. Sandstone lenses sometimes appear amid conglomerates. The clastic matter of conglomerates comes from two sources: local (volcanogenic rocks, sandstones, shales, jaspers, and limestones, indicating a differentiation of sedimentation basin topography) and allochthonous (granite and quartz material, apparently supplied from the shelf). The conglomerates are not layered. At different horizons they contain blocks and exotic broken fragments of the same limestones as in Karakatty olistostromes (massive layered limestones of various colors and carbonate breccias). Trilobites of the Middle and Upper Cambrian age and Ordovician brachiopods have been collected in them.

In the northern slope of the Karakatty ridge the Dolon mixtite bed has a different structure while retaining the overall general sequence. Conglomerate horizons alternate with members of green siltstone, which include lens-shaped interlayers of small-grained rust-colored sandstone. The conglomerates alternate rhythmically with sandstones. The rhythmicity is mostly symmetrical and sometimes pendular.

Sandstone interlayers in siltstone exhibit no sorted stratification. At the base of such interlayers traces of erosion of underlying siltstones are sometimes seen. Gradational stratification is rare. This pattern of the terrigenous bed suggests a transportation of material by grain flows and less often by suspension flows.

In the Dzhungal ridge, limestone and chert blocks are enclosed in tuffosandstone, tuffogritstone, and tuffoconglomerate. This complex of rocks is characteristic of a facies of submarine volcanic slope consisting of tephrogenic turbidites and fluxoturbidites with horizons of slump-landslide breccias. Carbonate and silicic horizons were formed on volcanic structures. Volcanic and seismotectonic activity led to a decay of the structure and the migration of coarse clastic material down the slope to the foot as a result of slumps and landslides.

In the Kirghiz ridge the slump-landslide olistostrome units proper are found at the center of the ridge and consist of massive conglomerate breccias with rare carbonate olistolites 100-150 m long and 20-30 m wide, and large amounts of effusive, schist, and granodiorite blocks.

Two types of olistostromes identified in the Lower Paleozoic of the northern Tien Shan correspond to the two different genetic types described by Leonov [13]:

Tectonogravitational mixtites of the Karakatty type were formed by disintegration of pre-Arenigian tectonic cover, charriages, and transportation of disintegrated material by underwater slumps. The processes occurred in environments of active seismicity associated with overthrusts. Carbonate breccias of a tectonic origin are evidence of this. Such olistostromes are an indicator of the horizontal movement of rock masses.

During the pre-Middle Arenigian, intense tectonic activity with formation of submarine ledges and cordilleras was established. Their collapse, the landslides, and the autokinetic flows that resulted provided material from which Dolon gravitational mixtites were formed. Large blocks are situated in the proximal parts of submarine alluvial cones.

* * *

Two stages can be clearly identified in the sedimentation history of the northern Tien Shan's Early Paleozoic basin. The first stage is the time of development of the formation of hemipelagic sediments with horizons of turbidites, fluxoturbidites, and edaphogenic breccias, and the contemporaneous formations of theoleiitic and andesitic basalts and the terrigenous formation with cherts. The time of their accumulation spans the Cambrian and the Tremadocian. The second stage (starting from the Arenigian) was the development epoch of olistostromal beds which preceded directly the accumulation of a thick flysch formation of the Middle Arenigian, Llanvirnian, and Llandeilian, not discussed in this paper.

Carbonate formations with a silicic-phosphoritic formation at the base accumulated on the shelf during the Early Paleozoic, while at the foot of the continental slope the terrigenous formation with cherts was accumulated. The basins had a fairly complicated morphology. They were isolated deep-sea depressions in which hemipelagic clay, clay-silicic, and silicic ooze accumulated. The absence of carbonate rocks in the profiles of these complexes, despite the

fact that carbonate accumulation was the principal sedimentary process in the shelf zone (Tamanda series of the Talas-Karatau zone), is proof that sediments accumulated beneath the level of carbonate compensation in the Early Paleozoic, which in Recent basins lies at a depth of 4.6 km and near continents at 3-3.5 km [27]. The textures and structures of the sediments forming the rock association suggest that they were created by deep-sea depression was compounded by local rises of a tectonic and volcanic origin, which affected sedimentation, supplying into the basin volcanoclastic graywacke and silicic detrital material. They were brought into the sediment burial zone by landslides and grain flows and, to a lesser extent, turbidity flows that developed on slopes of these rises. No influence of an influx of sialic clastic material from the continent is observed here, with rare exceptions, suggesting a large size of the deep-sea basin and its remoteness from the continent.

Deep-sea basins were conjugated with long belts of volcanic structures rising above them.

In practically all areas of northern Tien Shan, remains of pre-Arenigian tectonic cover charriaged into volcanogenic and volcanogenic-sedimentary complexes have been preserved. One can judge about the composition of the constituent rocks of the tectonic cover by almost intact relicts — Karakatty olistostromes and carbonate rock blocks in Dolon olistostromes.

Judging by benthic fauna remains and Arenigian graptolites found in overlying layers, the carbonate age is defined by the interval $\epsilon_2 + O_1$. This is also the age of volcanogenic and volcanogenic-sedimentary formations, into which the carbonate plates were charriaged. This means that carbonate accumulation areas were separate facies zones that coexisted with other zones. Their position in the sedimentation basin is inclear, because locations of their autochthonous occurrence have not yet been found. These could be shelf zones to the southwest of deep-sea sedimentation, tanks, areas of inner rises (Makbal-Burkhan) with sialic crust, and volcanic structures.

The formation time of olistostromal beds of the Early Arenigian dates the beginning of tectonic twisting, which resulted in the closure of the early geosynclinal structure of northern Tien Shan. The process was accompanied by the first intrusive magmatism (granodiorites, quartzose diorites and monzonites, plagiogranites or Nogaisai and Almaly Early Ordovician complexes). The twisting and charriage produced a strongly separated topography of the basin floor, where cordilleras were conjugated with remnant deep-sea basins) thick flysch strata of Middle Arenigian-Llanvirnian-Llandeillian accumulated in these basins, starting from Dolon gravitational olistostromes. The leading processes in their formation were submarine slumps and spread of material by turbidity and grain flows. Sialic matter appears in abundance in clastics (granites, quartzites, and various shales), showing that the sedimentation zone moved closer to the continental shelf. This process resulted in the spatial approach and charriaging of the different-facies complexes of the Early Paleozoic observed in the Recent structure of northern Tien Shan. The formations of $\epsilon + O_1$ have been transformed into a narrow strip with a high degree of twisting and appear as a packet of tectonic plates with different formational fillings.

The structural specifics of the volcanogenic-sedimentary profiles and their spatial interrelationships indicate a zonal differentiation of the Lower Paleozoic of northern Tien Shan, which allows reconstructing a large marine basin with hemipelagic sedimentation, shoals with belts of volcanic structures and carbonate sedimentation. Typical formational series of the western part of northern Tien Shan can be identified with the principal paleogeographic elements of a passive continental margin-shelf, continental slope, and the foot of the continental slope.

The alternation of the structures with suboceanic and continental types of earth's crust, the type of sedimentary process, and volcanic activity warrant comparing the ancient structure of the Kirghiz-Terskel zone of northern Tien Shan to the Recent marginal sea areas, such as the Philippine or Japan Seas.

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A NEW TYPE OF ZEOLITE OF VOLCANIC-LIMNIC ORIGIN (SOUTHERN MONGOLIA)

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UDC 553.67(517)

The lithology, mineralogy, and origin of two major zeolite occurrences discovered in the Mongolian Peoples Republic are described. The properties of the most important zeolite, clinoptilite, and the associated minerals are described. The mechanism whereby the deposits were formed is discussed.

A directed search for zeolitoliths in the Mongolian Peoples Republic was undertaken in 1984 by the Soviet-Mongolian Joint Geological Expedition at the initiative of A. G. Kossovskaya [5]. An essential first step for organizing the operation was to analyze the historical geology of the MPR. The volcanic sedimentary rocks of the Tsagan-Tsabsk suite (J_3-K_1cc) widely distributed over the entire territory of the MPR were originally selected as offering the greatest promise of hosting zeolite formations. This selection was based on data from earlier investigators [2, 8, 11, 12, et al.] who had shown that during the Upper Jurassic-Lower Cretaceous periods there was intensive volcanic mountain-building with the accumulation of thick extrusive flows in the east, the northeast, the center, and the south of this region. Because this region was covered at that time by large isolated lake basins of different degrees of salinity, the extrusion occurred under water at a number of localities, and the glassy material was able to accumulate in the lake basins. This created favorable conditions for the breakdown of the reactive glass and the formation of authigenic minerals. In particular zeolites, from its constituents. Other possibilities for zeolite formation were also envisaged, such as a) the direct chemical precipitation of zeolites from the mineralizing waters of the paleolakes; b) the formation of zeolite mineralization during the diagenetic aging of the volcanic-sedimentary material; and c) the hydrothermal synthesis of zeolites.

The very first seasons in the field in 1983-1984 resulted in the discovery of zeolites of significant areal extent and thickness [5]. This article deals with the peculiarities of the origin and authigenic mineralogy of two of these localities.

LITHOLOGY OF THE SECTIONS AND THEIR AUTHIGENIC MINERALS

Both zeolite occurrences, at Tushleg and at Tsagan-Tsab, are situated in the East Gobi aimak, the first 12 km to the south, and the second 30 km to the southwest of city of Sain-Shand, the aimak center. The zeolitized rocks outcrop as a series of low hills (15-20 m at Tushleg and 4-6 m at Tsagan-Tsab) of white and greenish-white color consisting of interlayered sedimentary, sedimentary-volcanic, and volcanic-sedimentary rocks. At Tushleg three unconnected sections are observed: an eastern, a southeastern, and a western. In this article we discuss the composition and structure of only the eastern section, an area of about 1×3 km. The area of the Tsagan-Tsab zeolite occurrence is 1.5×1.5 km.

The geological age of the sediments comprising the two zeolite occurrences has been fairly well determined on the basis of the fauna. It corresponds to the Tsagan-Tsab ($J_3^3-K_1cc$) and Shinkhuduk (K_1ssh) suites found in Southern Mongolia [2, 3, 12]. On the basis of a paleogeographic reconstruction of the historical development of the MPR at that time, V. F. Shuvalov [12] distinguished the following major features of the region.

1. The major geological structures were inherited from earlier developmental stages of the region and are characterized by the existence of mountain structures and inter- and intra-

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montane depressions. Tectonic movement during Tsagan-Tsab time complicated the structure of some of the elevations, rejuvenating old ones and giving rise to new volcanic structures, and caused the expansion of many previously existing depressions and the appearance of new ones, small in area and shallow in depth.

2. The relief of the region is gradually reduced from Tsagan-Tsab to Shinkhuduk times. Toward the end of the epoch, mountainous structures remained only in the most elevated axial parts.

3. The climate was not uniform, relatively humid epochs alternating with more arid; seasonal variations in the weather were observed.

4. The majority of the depressions were occupied by basins having either internal or external drainage, having either fresh or slightly saline water. The major type of sedimentation was limnic.

5. The tectonic movements, the rugged terrain, and the well developed drainage network contributed in the early periods of Tsagan-Tsab time to the accumulation of coarse clastic material in the sedimentary basins, which gradually gives way in the sections to the psephitic and psammitic sediment types predominating in the sections and containing in the later stages (upper Tsagan-Tsab—lower Shinkhuduk age) thin lenses and local interbeds of conglomerates.

6. Active volcanoes throughout the entire Neocomian stage supplied the sedimentary basins with abundant tuff material.

These features are distinctly seen in specific lithological sections of the two zeolite occurrences. The rhythmic structure of the sequences, the areal persistence of even the thin interbeds, their circular-isometric distribution, and the presence of fine layering provides evidence of the limnic nature of the sedimentation of these sections. The lithological composition of the sediments, the distribution of the material, and the species composition of the fauna provide the grounds for assuming that despite the fact that sedimentary basins of contemporary zeolite occurrences were not connected, sedimentation began in each of them with coarse clastic material and the formation of tuffaceous-sedimentary sequences reflecting the nature of the accumulation of the material of early Tsagan-Tsab time. The later, tectonically more tranquil history of the region saw the accumulation of sedimentary-tuffaceous sequences in the sections, which at Tsagan-Tsab are not only thicker than at Tushleg, but significantly more saturated with volcanic (tuff) material. The concluding stages of sedimentation in both areas are again characterized by an increased supply of clastic material, but the conglomerate interbeds at the Tsagan-Tsab—Shinkhuduk boundary are found only in the Tushleg section. At Tsagan-Tsab, accumulations of coarse tuff-sandstones are noted at this time. In Shinkhuduk time, thin tuffaceous-sedimentary sequences were formed in both sections.

It should be noted that during subsequent stages in the development of the region, the rocks of the Shinkhuduk suite in this region were not covered by younger sediments.

In each of the sections the sequence is subdivided into a number of members. A detailed description of the lithology and mineralogy of these members is given separately for each zeolite locality.

Tsagan-Tsab. The lithological column of this locality is shown in Fig. 1a. Its description from bottom to top, from the older Tsagan-Tsab rocks (members I-VII) to the younger (member VIII) is given below.

The lower tuffaceous-sedimentary sequence includes members I-IV and characterizes the stage of accumulation at the bottom of the section of coarse clastic material with interbeds of tuff-sandstones, tuff-siltstones, and tuff-argillites and fairly thick, sometimes lenticular interbeds of tuffites.

Member I — interstratified conglomerates, gravelstones, sandstones, argillites, some tuffites and tuff-sandstones. The sedimentary material is well rounded and is represented in the sandstones by quartz, plagioclase, potash feldspar, flakes of biotite, and fragments of extrusive rocks; in the gravelstones and conglomerates there are also fragments of intrusive and metamorphic rocks; the cement is interstitial and contact-type, smectite-hydromicaceous with a small amount of carbonate, or carbonate-clay. The zeolites, which account for up to 35% of the volume of the rock, are encountered only in the tuffaceous varieties. The total thickness of the member is as much as 10 m, the thickness of the individual interbeds is from 0.1 to 3 m.

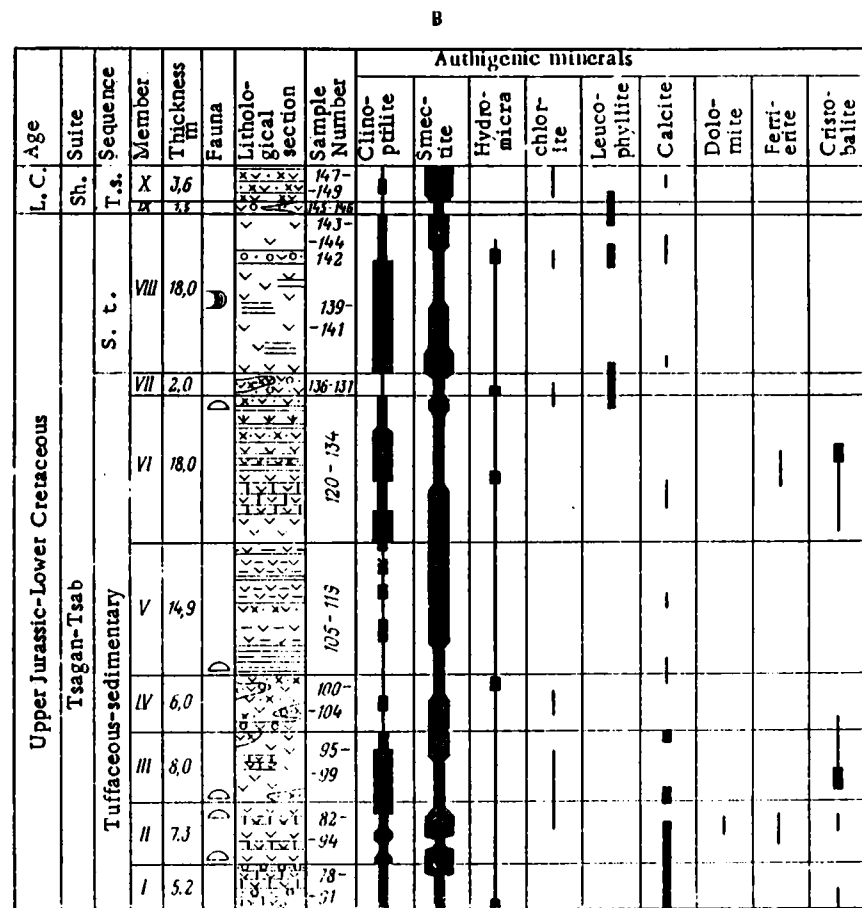
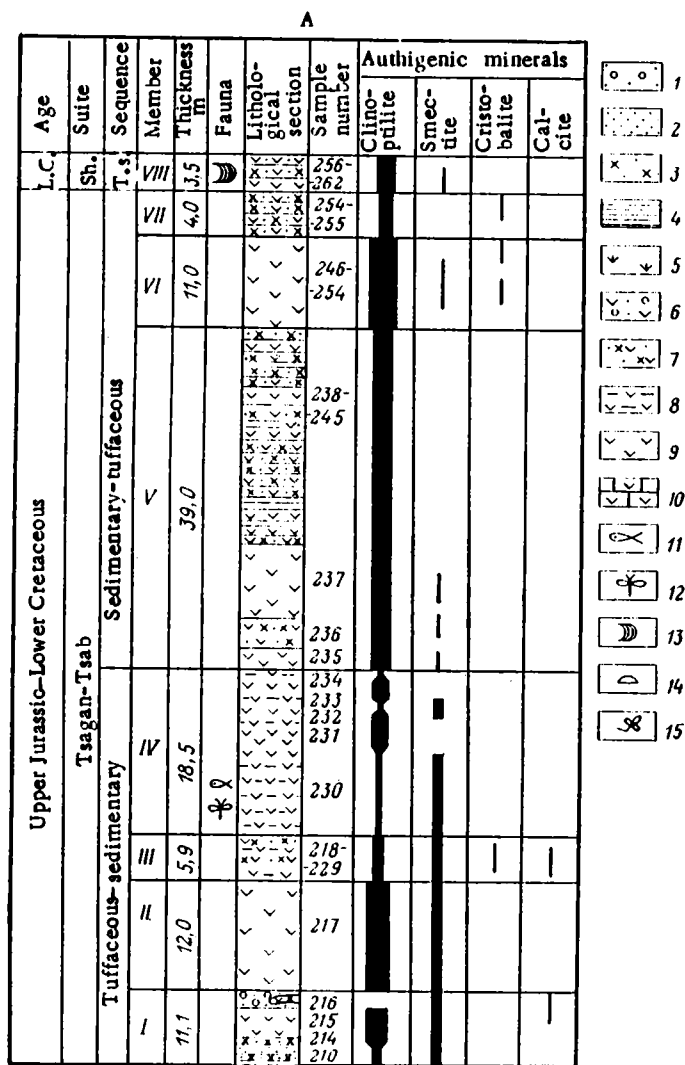


TABLE 1. Chemical Composition of Zeolitized Tuffites, wt. %

Oxide	Tsagan-Tsab								Tushleg		
	I (3)	II (2)	III (1)	IV (1)	V (3)	VI (4)	VII (1)	VIII (3)	III (1)	VIII (2)	X (1)
SiO ₂	63.69	63.54	63.80	64.59	65.09	63.84	69.06	64.58	63.55	67.33	63.64
TiO ₂	0.21	0.21	0.30	0.29	0.18	0.20	0.17	0.21	0.25	0.25	0.29
Al ₂ O ₃	12.55	12.30	13.53	14.29	12.76	12.04	12.13	14.38	12.39	11.97	14.20
Fe ₂ O ₃	2.11	0.87	2.69	0.44	1.34	2.82	0.79	0.64	1.44	1.65	1.82
FeO	0.35	0.25	0.14	0.35	0.18	0.22	0.18	0.24	0.38	0.20	0.29
CaO	1.47	2.43	2.66	2.45	2.36	1.83	2.31	2.96	4.56	1.93	3.13
MgO	1.74	1.41	0.88	0.92	1.09	1.00	0.50	1.34	2.05	2.34	1.90
MnO	0.01	0.01	Trace	0.01	0.01	0.01	Trace	0.25	0.01	0.02	0.01
Na ₂ O	2.80	3.16	3.43	4.70	3.27	3.00	3.61	4.16	1.88	1.20	2.70
K ₂ O	2.87	2.86	3.44	3.29	3.34	3.52	3.33	3.86	4.00	4.42	2.87
H ₂ O ⁺	6.24	6.66	4.09	4.88	5.06	5.42	3.52	3.84	5.15	4.08	4.56
H ₂ O ⁻	6.06	5.64	4.42	3.42	5.02	5.79	3.74	2.14	3.61	4.06	3.91
P ₂ O ₅	0.06	0.04	0.12	0.01	0.04	0.01	0.01	0.04	0.06	0.03	0.02
	100.07	99.38	99.50	99.64	99.74	99.70	99.44	99.64	99.33	99.48	99.34

Note. The analyses were made using wet chemical techniques (the analysts were E. V. Cherkasova and N. L. Kalashnikova); the Roman numerals indicate the number of the member, the numbers in parentheses are the numbers of analyses.

TABLE 2. Major Chemical Components of the Authigenic Minerals

	Tsagan-Tsab			Tushleg			
	281 (9)	249 (3)	97 (1)	84 (8)	84a (5)	136 (3)	99 (2)
SiO ₂	67.38	68.19	76.22	63.22	64.17	54.53	64.37
Al ₂ O ₃	12.23	12.66	14.49	12.35	11.39	12.37	16.27
Fe ₂ O ₃	0.20	Trace	0.04	0.08	Trace	4.99	4.39
MgO	0.50	0.61	0.80	1.10	2.73	5.70	4.14
CaO	2.17	2.05	2.07	2.76	0.63	0.04	0.96
Na ₂ O	0.41	0.30	0.10	0.88	0.09	2.01	0.04
K ₂ O	1.23	0.87	2.83	1.95	0.82	7.84	2.10

Note. The analyses were made on a Kamebaks microanalyzer (the analysts were G. V. Karpova and V. G. Senin). Samples 281, 249, 97, and 84 are clinoptilite; sample 84a is ferrierite; sample 136 is leucophyllite; 99 is smectite; the number of analyses is given in parentheses.

Member II—psephitic-psammitic vitroclastic tuffite, with quartz, plagioclase, biotite, and fragments of effusive rocks. The content of the clastic component is 5-15%. The glass is zeolitized, smetitized, and carbonatized. The zeolite content is about 35% of the volume of the rock. Infrequent, thin interbeds of tuff-sandstone are noted. The total thickness of the member is as high as 20 m.

Member III — thin interstratified members of tuff-sandstones, tuff-siltstones, and tuff-argillites. Clasts are poorly rounded and consist of quartz, feldspars, and biotite; hornblende and apatite are encountered. The cement is pore-filling and occupies up to 40% of the volume of the rock. There are phosphorites, Fe-Mn ore segregations, and plant fossils. The glass of the volcanic component is altered to smectite, carbonate, and zeolite. Zeolite is also noted in the pore spaces. The total content of the zeolite amounts to 15% of the volume of the rock. The thickness of the member is about 6 m; the thickness of the individual interbeds varies from a few millimeters to 2 m.

Member IV — interstratified, compacted tuff-argillites with fine slaty cleavage and tuffites. The tuff-argillites are smectitic, weakly carbonate, with a varved texture; they contain fine quartz, mica, and glass clastic material coated with organic matter. In the tuffite the content of the sedimentary component is about 40%. The clastic material is almost unrounded and consists of quartz, plagioclase, and biotite. The volcanic component is glass altered to zeolite. The zeolite content accounts for 30-40% of the rock volume. The total thickness of the member is up to 20 m. The thickness of the individual strata varies from a few centimeters to 10 m.

The central sedimentary-tuff sequence includes members V-VII and represents the stage of intensive accumulation of sedimentary-volcanic material under unvarying conditions; it is represented by interstratified tuffites and tuff-sandstones.

Member V — interstratified tuffites, tuff-sandstones, and compacted tuff-siltstones. Characteristic of the tuffite is a fine-layered texture expressed in the alternation of beds differing in granulometric and compositional makeup. The beds are areally persistent; only in places are the layers disrupted. The tuffite is vitroclastic; the sedimentary component varies from 5 to 40%. The clastic component includes quartz, plagioclase, less frequently fragments of effusive rocks and quartzites; zircon grains are encountered; apatite is present. The tuff-sandstone is feldspathoquartzitic with a large amount of extrusive rock, at times altered; biotite, pyroxene, and hornblende are present. The amounts of the clastic and volcanic components are approximately equal. The glass is altered to zeolite; zeolite is infrequently observed in pore spaces.

The thickness of the individual strata varies from a few millimeters to a few meters. The thickest strata may reach 12 m.

Member VI — vitroclastic tuffite with fragments of quartz, plagioclase, biotite, more rarely zircon, apatite, and sphene. The amount of quartz and alkali minerals increases in the upper part of the section. The content of sedimentary material accounts for 5-10, infrequently up to 20% of the rock. The banded texture of the tuffite caused by the alternation of layers of differing granulometric composition is complicated by spheroidal parting characteristic of tuffites containing the smallest amounts of sedimentary material. It can be assumed that the ash experienced minimal transport and fell into the water immediately after ejection, which is what was responsible for the formation of the spheroidal parting as it underwent compaction. The vitroclastic composition of the member also is responsible for its having experienced the greatest alteration. The content of zeolite in it is 60-80%, the highest in the section. The total thickness of the member is up to 20 m.

Member VII — tuff-sandstone. The content of the sedimentary material is 50-60%. The clastic material is more rounded than in the previous members, and contains significantly less biotite. The glass of the volcanic component is altered to zeolite and smectite. The content of zeolite is 30-40% of the rock by volume. The thickness of the member is about 5 m. The tuff-sandstone is threaded by a network of later fissures, oriented perpendicular to the direction of the bedding. The fissures are filled with quartz and manganese hydroxides.

The thin upper tuff-sedimentary sequence is represented by one member (VIII) and contains fresh-water fauna of the Shinkhuduk horizon.

Member VIII — interstratified tuffites and tuff-sandstones. Poorly rounded quartz fragments (quartzite, chalcedony), feldspar (plagioclase, potash feldspar), more rarely biotite, pyroxene, epidote, and extrusive rocks account for 60% of the tuff-sandstones. The glass of the volcanic part is altered to zeolite and smectite. The total zeolite content is up to 30%. In the upper parts of the section, the tuff-sandstones are intensely iron coated and contain a small amount of manganese. The tuffites are pelitic and have silt-size particles. The clastic content is 5-10%, rarely as high as 40%. Its composition: quartz, plagioclase, and biotite. The volcanic component is vitroclastic tuff. The glass is altered to zeolite. The zeolite content varies between 20 and 60%, decreasing in the upper parts of the section. The thickness of the member is up to 7 m; the individual beds are from a few centimeters to 3 m thick.

On the whole, the zeolite content in the rocks of the section amounts to 10 to 80% of the total. Large amounts are noted in the tuff varieties, the maximum amount being observed in the tuffites of member VI.

The zeolites of the entire region are fairly uniform in chemical composition (Table 1). The SiO_2 content averages 62-64%, rising to 69% in weakly silicified tuffites close to tectonic disturbances. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio varies from 4.14 to 6.40. The amounts of CaO , Na_2O , and K_2O are approximately equal (cf. Table 1). These values are comparable to the chemical compositions of the zeolites from the Geizer deposits on Kamchatka and the Krainikovo deposit in Transcarpathia, since the overall composition of the Mongolian rocks is affected by the original, undecomposed glass and the terrigenous material present in the tuffites hosting the zeolites. The NaO_2 content in particular is sharply higher in the zeolitoliths than in the pure zeolite (Table 2). For this reason the end-use properties of the Mongolian zeolites may differ considerably from those of zeolites from the USSR.

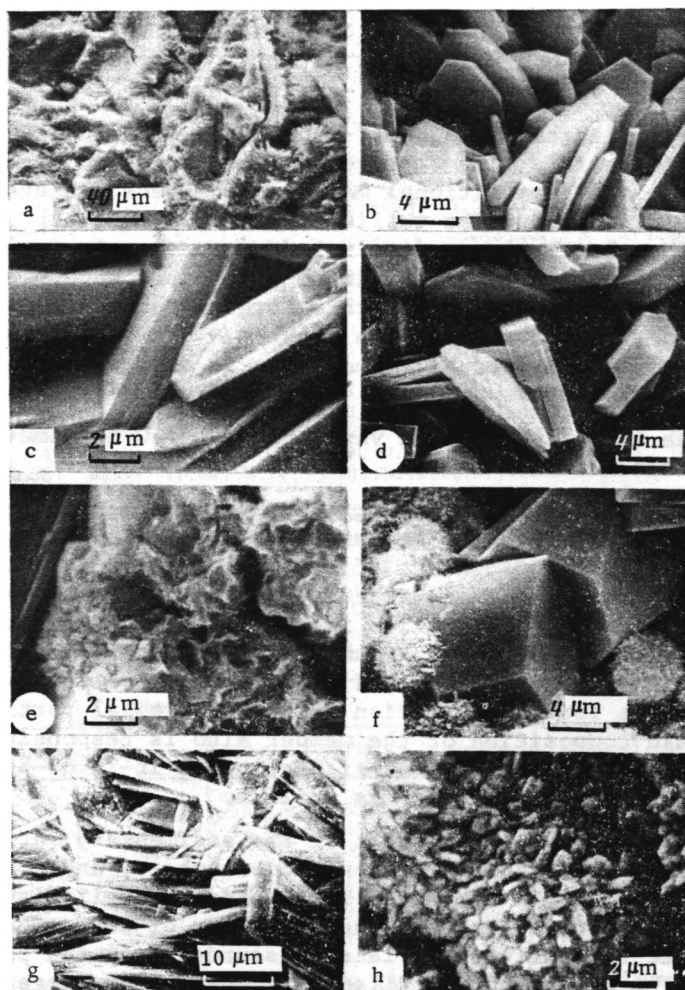


Fig. 2. Morphology of authigenic minerals of the zeolitoliths (scanning electron microscope). a) clinoptililite pseudomorphs of volcanic glass; b-d) morphological varieties of clinoptililite crystals: e-f) replacement of stubby prismatic clinoptililite crystals (e — by smectite and ferrierite, f — by ferrierite); g, h) morphological varieties of ferrierite (a-d — Tsagan-Tsab; e-h — Tushleg).

Authigenic Minerals. The only zeolite identified at Tsagan-Tsab is clinoptililite. On the basis of morphology and origin there are distinguished platy (Fig. 2b; 3h), short- and long-prismatic crystals (cf. Fig. 2c and d) that grow in the open micropore spaces, and the cryptocrystalline aggregates forming pseudomorphs after the glass (cf. Fig. 3f). Both types give distinct x-ray diffraction patterns of clinoptililite (Fig. 4), but the diffraction diagrams for the cryptocrystalline variety contain a larger number of the hk reflections. The intensities of the reflections of $[020]$ with $d = 8.9 \text{ \AA}$ vary considerably depending on the morphological features of the crystals, as do the poorly resolved groups of reflexes with the indices $[132]$, $[004]$, and $[042]$, which merge into one broad peak with $d \approx 3.93 \text{ \AA}$. The highest intensity for the $[020]$ reflection is characteristic of clinoptililites with the platy crystal habit, while for the cryptocrystalline or stubby-prismatic varieties the intensity of the $[020]$ reflection and the average reflection with $d \approx 3.93 \text{ \AA}$ may be equal, or the latter may become the stronger. Clinoptililite is thermally stable and can withstand heating at 550°C for 15 h, and an additional 2 h of heating at 700°C without any change in the x-ray diffraction pattern.

On the basis of its cation composition, the clinoptililite is a Ca-K variety containing a small amount of Na (cf. Table 2). The Si/Al ratio is between 4.38 and 4.87. The variation in the content of the individual components is considerable, however, and amounts to, in weight %: SiO_2 62.7–72.5; Al_2O_3 11.5–13.4; MgO 0.31–0.61; CaO 1.63–2.80; Na_2O 0.08–0.61; K_2O 0.76–2.06. These variations are observed even within a single crystal, and it is possible to de-

fect only a weak tendency for the silica content to increase in the largest crystals. The amount of water in the clinoptilite varies from 5.5 to 11%, this being associated with both water of crystallization and sorbed water, according to an analysis of its IR spectra and thermal curves.

Thus, the Tsagan-Tsab clinoptilite exhibits the properties typical of this mineral, and in the practical application of the Tsagan-Tsab zeolitoliths the specific nature of its Ca-K cation composition should be taken into account, rather than the overall composition of the rocks.

At the Tsagan-Tsab locality, clinoptilite is the major authigenic mineral (cf. Fig. 1a). Sporadically throughout the section and over the area of the deposit, smectite, cristobalite, and calcite are noted in a paragenetic assemblage with it. (Since the amount of these minerals is small, they could be detected only by their x-ray diffraction patterns.

Smectite develops from the original glass of the tuffites, generally in the lower part of the section and at its very top. In the x-ray powder diffraction diagrams of the smectite, the 060 reflection is within the angular interval corresponding to $d = 1.496 \text{ \AA}$, indicating the dioctahedral variety of the mineral. The d value of the small angle basal reflection 001 varies within the limits 11.6-14 $\text{\AA}$, which corresponds to the K-Na, Ca-Na, and Ca-forms of smectite.

Cristobalite (opal CT) is encountered primarily in tectonically disturbed parts of the section in selvage fissures filled with quartz. In some instances, rims of cristobalite are observed on the surfaces of grains of terrigenous quartz. The [101] reflection recorded on the diffraction patterns with a d value of 4.04-4.08 $\text{\AA}$ corresponds to the low-temperature variety of the mineral.

Calcite is rare. In most cases it cements the grains and rock fragments in tuff-sandstones, tuff-gravelstones, and conglomerates. In rare instances it replaces glass previously altered to clinoptilite and smectite.

Also noted among the late minerals in the Tsagan-Tsab region were gypsum, halite, and phosphates, but these are restricted to parts of the section enriched in terrigenous material and are of clearly exotic; they are not found in the clinoptilite paragenesis, and are therefore not considered in this article.

Tushleg. As in the previous case, in this section of the altered to zeolite rocks (cf. Fig. 1b) three sequences can also be distinguished: two tuffaceous-sedimentary (members I-VII and IX-X) and a sedimentary-tuff sequence separating them (member VIII). The description of the members is from the bottom upwards, from the older Tsagan-Tsab (members I-VIII) to the younger Shinkhuduk (members IX-X) deposits. The age of the sediments was determined from the ostracod fossils widely distributed throughout them.

Member I — a conglomerate with interbeds of carbonatized (to 90%) tuffites. The tuffite is vitroclastic quartz-plagioclase with rare extrusive fragments. The zeolite content is about 10% of the rock volume. The member is 5.2 m thick.

Member II — interstratified light-green and light-grey carbonatized tuffites with fine interbeds of clay (up to 0.1 m) and tuff-sandstones (up to 0.2 m). The mineral composition of the tuffites is: quartz, plagioclase, and fragments of extrusive and intrusive rocks, embedded in glass altered to zeolite, smectite, and hydromica. The sedimentary component content is 40-50%. The average zeolite content is 15% of the rock volume. Carbonate alteration of the rock is a late process. Calcite and in rare instances dolomite is developed from all the components of the rock, including the zeolites. The total thickness of the member is 7.3 m.

Member III — a greyish-white tuffite, vitroclastic with quartz, plagioclase, biotite, and fragments of extrusive and intrusive rocks. The texture of the tuffite is spherulitic. The size of the spherules varies from 3 to 50 cm in diameter, with spherules of 15-25 cm predominating. The external zone of the spherules is friable, conchoidal, and has been altered to carbonate; the interior is dense and altered to zeolite. Within the member are observed individual interbeds of dense grey-green tuffites (up to 0.1 m thick), tuff-gravelstones (up to 0.3 m thick), and tuff-sandstones (up to 0.2 m thick). The average zeolite content is up to 20%. The overall thickness of the member is 8 m.

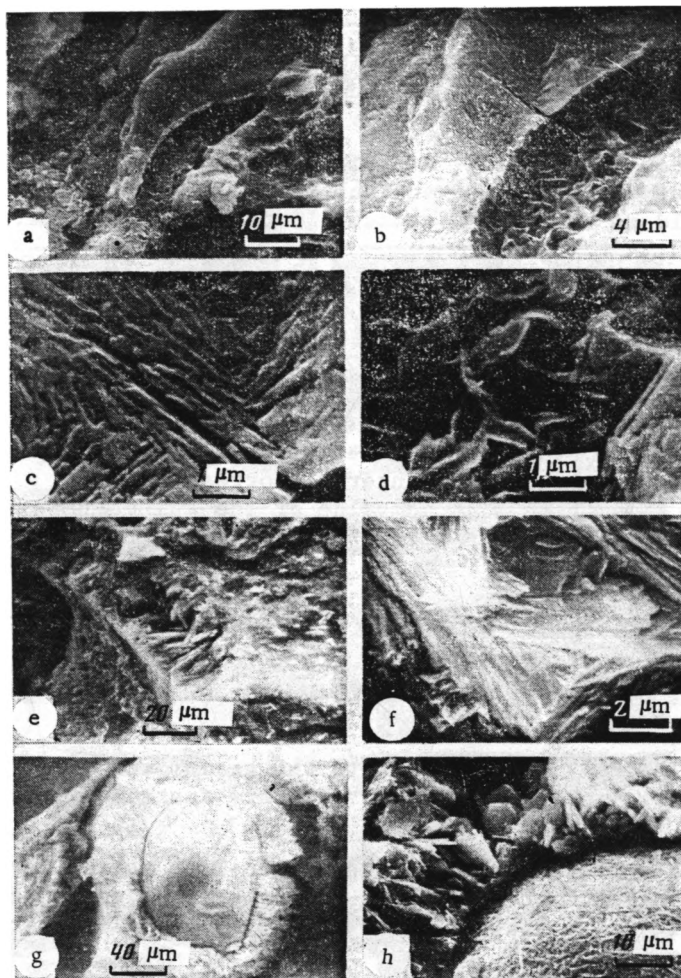


Fig. 3. Characteristic features of the zeolitization of volcanic glass (scanning electron microscope). 1) section of a zeolitized tuffite at $\times 2000$ (the horn shape of the original glass is clearly visible); b) the same at $\times 5000$; the "unevenness" on the surface of the glass can be seen; c) the same at $\times 20,000$; it can be seen that the "unevenness" is from complete pseudomorphic crystals of zeolite developed from the glass; d) the same, at $\times 20,000$, crystals of smectite in a micropore space; e) replacement of glass by clinoptililite with the growth of individual crystals in pore space; f) cryptocrystalline aggregates of clinoptililite developed from glass; g) development of zeolite margins around a quartz grain; h) the same, larger, crystals of clinoptililite are clearly visible surrounding the quartz surface altered to cristobalite

Member IV — a conglomerate with interbeds of quartz-plagioclase sandstones and psephite vitroclastic tuffites. The content of fragmental material in the tuffite is 40%; its composition includes quartz, plagioclase, opal, and chalcedony. The glass is altered to zeolite and smectite. The zeolite content is up to 10%. The thickness of the individual interbeds is up to 1 m. The member is 6 m thick.

Member V — interstratified grey-green tuff-siltstones and blue-grey argillitic rocks. Interbeds of tuff-sandstones are encountered. The tuff-siltstone is quartzoplagioclasic, in places with fragments of extrusive rocks. The content of the sedimentary component is 50-60%. The volcanic part is glass altered to smectite, partially to zeolite, rarely carbonatized. The zeolite content is 15-20%. The tuff-sandstone is quartzoplagioclasic with fragments of extrusive rocks; biotite and epidote are encountered. The cement is glass altered to smectite or partially altered to zeolite, in places to carbonate. The zeolite content is 15-30%. The clay is a smectite-hydromica variety. The hydromica particles are frequently oriented, im-

TABLE 3. Calculated (I) and Observed (II) X-Ray Values for Ferrierites

hkl	British Columbia [16]			hkl	MPR		
	d, Å		I		d, Å		I
	I	II			I	II	
110	11.38	11.33	2	—	—	—	—
200	9.56	9.61	10	—	9.48	9.4	10
020	7.07	7.00	3	020	7.04	—	—
101	6.97	—	—	101	7.00	6.98	2
011	6.61	6.61	2	011	6.65	—	—
310	5.81	5.84	5	310	5.76	5.75	2
220	5.68	—	—	220	5.65	—	—
211	5.44	—	—	211	5.44	—	—
121	4.96	4.96	1	121	4.96	4.94	1
301	4.85	—	—	301	4.84	—	—
400	4.78	4.80	1	400	4.74	4.74	2
—	—	—	—	311	4.58	4.58	1
130	4.57	4.58	1	130	4.55	—	—
321	4.00	—	—	321	3.99	—	—
031	3.99	3.99	9	031	3.98	—	—
420	3.96	—	—	420	3.93	3.93	3
411	3.87	3.88	1	411	3.86	—	—
330	3.79	3.79	2	002	3.77	—	—
002	3.74	—	—	330	3.768	3.77	2
510	3.69	3.69	5	231	3.67	3.67	2
231	3.68	—	—	510	3.66	—	—
112	3.55	—	—	112	3.57	—	—
040	3.53	3.54	8	040	3.52	3.52	4
202	3.48	3.49	8	202	3.50	—	—
501	3.41	3.42	2	501	3.39	—	—
240	3.32	3.31	2	240	3.30	3.30	2
600	3.19	3.20	1	600	3.16	3.17	3
141	3.15	3.15	3	312	3.15	—	—
312	3.14	—	—	141	3.14	—	—
—	—	—	—	610	3.08	3.06	1
521	3.07	3.07	3	351	3.05	—	—
431	3.06	—	—	—	—	—	—
530	2.97	2.97	3	—	—	—	—
402	2.95	—	—	402	2.95	2.97	1
—	—	—	—	322	2.94	—	—
620	2.90	—	—	620	2.90	—	—
132	2.896	2.90	2	132	2.88	2.89	1
341	2.85	—	—	341	2.85	2.85	1
422	2.719	2.72	2	422	2.72	2.72	1
631	2.645	2.64	2	—	—	—	—
502	—	—	—	502	2.67	2.68	1
642	2.57	2.58	3	—	—	—	—
End of data				540	2.58	2.58	1
				602	2.42	2.43	1
				640	2.35	2.35	2
				632	2.15	2.14	2
				603	1.967	1.967	1
				533	1.913	1.910	2
				723	1.782	1.786	2
				643	1.717	1.721	1
				724	1.588	1.592	2

Note. The x-ray diffraction diagram of the ferrierite from the MPR was indexed by S. I. Tsipurskii.

parting a slatey cleavage to the rock. The clays are 0.8-2.5 m thick, the tuff-siltstones are 1.2-1.7 m thick, and the tuff-sandstones are 0.2-0.5 m thick. The overall thickness of the member is 14.9 m.

Member VI — interstratified grey-green tuffites, blue-green clays, and brownish-grey or greyish-brown tuff-sandstones. The tuffite is vitroclastic with quartz, plagioclase, biotite, more rarely with hornblende, and with fragments of extrusive rocks. The content of the sedimentary component is 15-35%. The glass is altered to smectite and zeolite. The zeolite content is 10-30%. The tuff-sandstone is a greywacke, and the majority of the grains are well rounded. The cement is pore-filling, in places basal. The cement is glass altered to smectite and zeolite. The zeolite content is 1-20%. The clay developed from carbonates, in places hydromica, and slates. The thickness of the individual clay interbeds is 1-5 m, that of the tuffites and tuff-sandstones, 1-3 m. The member is 18 m thick.

Member VII — a poorly-sorted conglomerate with individual interbeds and lenses of tuffites, tuff-siltstones, and tuff-sandstones. The size of the pebbles is from 1 to 14 cm; well-

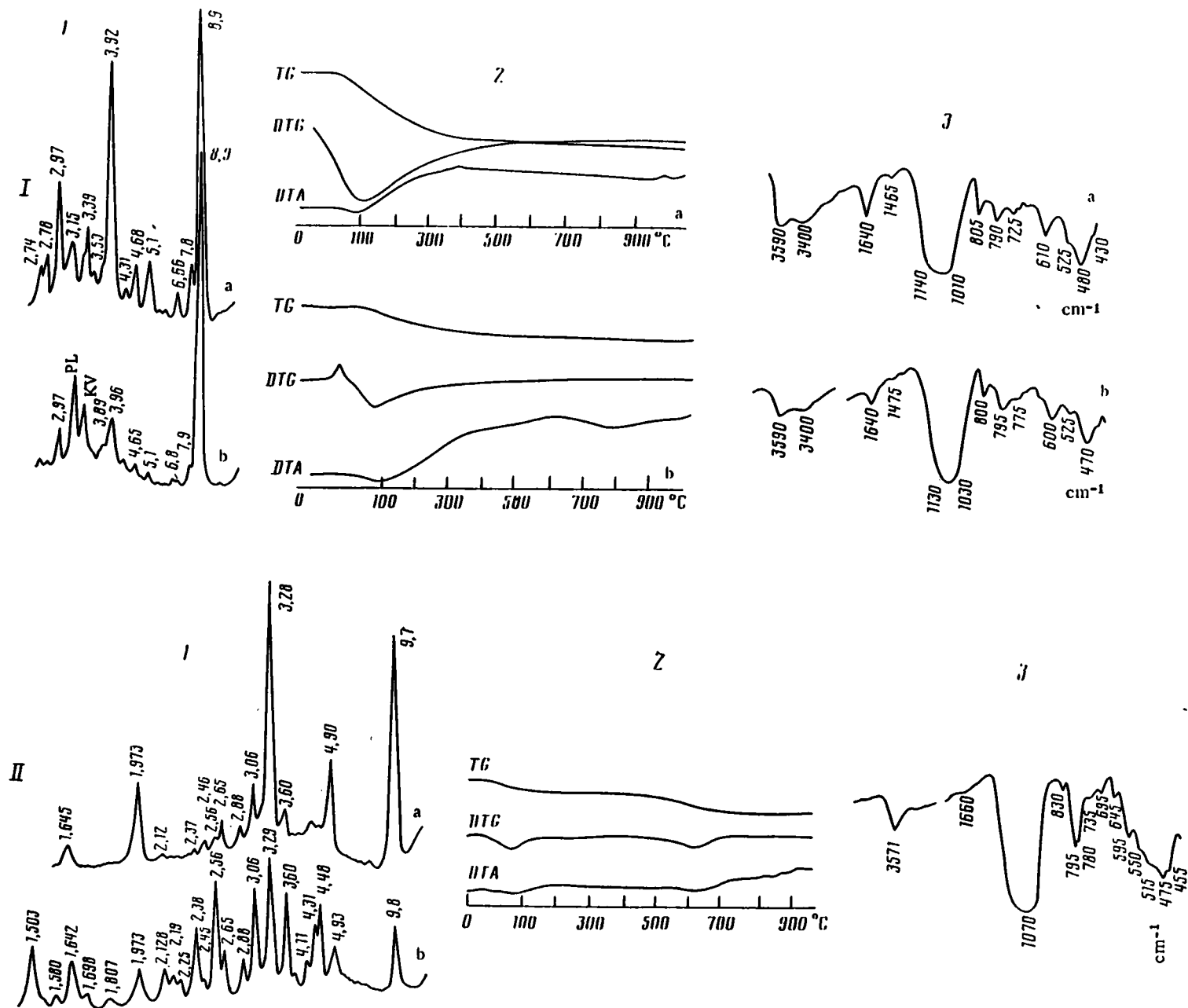


Fig. 4. Characteristics of the physical properties of clinoptilite and leucophyllite. 1) clinoptilite (a - cryptocrystalline; b - calcined at 550°C); 1 - X-ray diffraction diagrams; 2) thermograms; 3) IR-spectra.

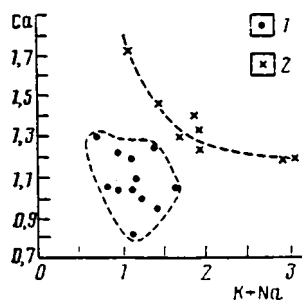


Fig. 5. Cation composition of the clinoptililite. 1) Tsagan-Tsab; 2) Tushleg (the amounts of Ca, K, and Na are given per 72 atoms of oxygen).

rounded pebbles 6 cm in size predominate. The composition of the pebbles, in %: granite 85, extrusives 10, and metamorphics 5. The cement is tuffitic. The ash particles of the glass in the tuffite are altered to leucoxene. The presence of this rare hydromica imparts to the entire stratum a dark green-blue color. The member is 2 m thick.

Member VIII — a tuffite with spherulitic texture, with individual fine interbeds and lenses of light blue-green argillitic clays, with conglomerate interbeds. The color of the tuffites varies upward from white to greyish-green. The tuffite is vitroclastic, with quartz, plagioclase, more rarely hornblende and zircon. The content of the clastic component is 15-40%. The glass is altered to smectite and zeolite. The zeolite content is 30-60%. At the top of the member the content of the sedimentary component is the tuffites increases to 50%, and the content of the zeolites decreases to 10-30%. The clay is a smectite-hydromicaceous variety. The conglomerate is poorly sorted with a cobble size of 3-18 cm; cobbles of 8 cm predominate. The rounding is slight. Composition, in %: granite 80, extrusive rocks 17, sedimentary rocks 3. The matrix is tuff-gravelstone and tuff-sandstone. In the matrix the zeolite content is no more than 5%. The individual interbeds are up to 0.3 m thick; the members 18 m thick.

Member IX — conglomerate. The cobble is poorly rounded, in places angular, up to 25 cm in size (average size 10 cm). Composition, in %: granite 70; extrusives 20, metamorphic rocks 6, and siliceous rocks 4. The matrix is sandy gravel with tuffite in places. The tuffite glass is altered with the formation of dark green-blue leucophyllite. The member is 1.5 m thick.

Member X — a tuff-sandstone with interbedded tuff-siltstones and clays. The tuff-sandstone is a greywacke (quartz, plagioclase, biotite, and fragments of extrusive, metamorphic, and igneous rocks, with a wide assortment of minerals such as tourmaline, epidote, and hornblende). The cement is porefilling-basal, represented by smectitized and altered to zeolite glass. The zeolite content is 5-30%. The tuffite is vitroclastic with quartz, more rarely with plagioclase. The content of the sedimentary component is 40%. The glass is altered to zeolite, later to carbonate. The zeolite content is 10%. The clay is a smectite-hydromica variety. The member is 3.6 m thick.

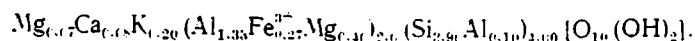
As at the Tsagan-Tsab site, the greatest amount of zeolite is restricted to the tuffite parts of the section, where they account for 30-60% of the total rock. The tuff-sedimentary varieties contain from 5 to 20% zeolites. The overall chemical composition of the altered to zeolite tuffites is given in Table 1. The SiO_2 content lies within the limits 63.5-69.1%; Al_2O_3 11.8-14.2%. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio varies from 4.4 to 5.8. The cation composition is not uniform and amounts to, in wt. %: CaO 1.6-4.6; Na_2O 1.0-2.7; K_2O 2.4-6.4. This scatter can apparently be explained by the lack of uniformity of the degree and type of transformation of the starting tuffite. As can be seen from the description of the sections, the major minerals that develop from the volcanic glass in the paragenesis with the zeolite are smectite, hydromica, and calcite. It is just these minerals that can affect the total content of such components as Ca, Mg, and K in the rock. Nevertheless, it is possible to note that in contrast to the Tsagan-Tsab zeolites, the Tushleg altered to zeolite tuffites are more siliceous and contain less Na and more K and Ca. We were unable to find zeolites from the USSR having a bulk chemical composition analogous to the Tushleg zeolites, which are distinguished by their high K_2O content.

Authigenic Minerals. Clinoptililite is the major zeolite at Tushleg. Two generations of the mineral are distinguished. The first, more widespread, formed from volcanic glass (cf. Fig. 3a-c), and more rarely in pore spaces (cf. Fig. 3f). The crystals of clinoptililite I bear the traces of dissolution or are partially replaced by carbonate, smectite (cf. Fig. 3e) and later zeolite present in the form of spherical aggregates of fine crystals (cf. Fig. 3f, h), the composition of which has not yet been identified. Such extensive replacement does not allow separation of the fractions that consist entirely of clinoptililite I. As a result, microprobe chemical analyses of the first generation of the clinoptililite are imprecise and show a wide scatter in the content of all the rock-forming components, in %: SiO_2 62.06-76.22; Al_2O_3 17.49-15.57; FeO 0.04-4.38; MgO 0.80-4.23; CaO 0.42-2.07; Na_2O 0.03-0.28; K_2O 0.24-2.83. The analysis that appears to us to be the most precise is that given in Table 2 for sample 97, a K-Ca variety of the mineral with subordinate amounts of Mg.

The second generation of the clinoptililite is later and is noted only in fissures and pore spaces of altered to zeolite tuffites that have undergone late carbonate alteration. Clinoptililite II is encountered in the form of pink platy crystals 1 mm in size and drusy encrustations of these. On the basis of their chemical analysis they belong to the Ca-K variety of the mineral with a Si/Al ratio of 4.2-4.8. The content of the rock-forming components, in %: SiO_2 60-66; Al_2O_3 12-13; CaO 2.3-3.5; K_2O 1.0-2.6; Na_2O 0.4-1.6. These variations are observed even within the limits of a single grain. An inverse correlation is noted between the content of Ca and Na + K in the unit cell (Fig. 5).

Ferrierite is noted in association with clinoptililite II. A detailed description of this rare Mg zeolite has been given by us earlier, so that in this article we shall mention only its most important characteristics. Ferrierite is encountered in the form of matted fibers or radial cotton-like aggregates consisting of fine bladed crystals whose length is tens of times greater than their width (cf. Fig. 2g). In thin sections, ferrierite is distinguishable by its double refraction, relatively strong for a zeolite (0.004), its index of refraction $N_g = 1.486$ -1.487; $N_p = 1.482$ -1.483, and by the nature of the striations that separate the compactly pressed crystals of ferrierite from each other and remind one of a double seam. The chemical composition of the ferrierite is given in Table 2. In comparison with the ferrierites found in other regions, that of Tushleg is rather low in silica (the silica content is from 57 to 64 wt %) and in alkalies, with K_2O predominant over Na_2O . The amount of MgO lies within the interval 2.5-3.1 wt %. The unit cell parameters ($a = 18.96$; $b = 14.08$; $c = 7.54$ Å) differ somewhat from the standard values: a and b are smaller, and c is larger. The difference in the unit cell dimensions also explains certain differences in the d values of the reflections in the diffraction diagrams of the mineral (Table 3).

Smectite is the most widespread of the authigenic minerals at Tushleg. It forms in all rock types and is encountered in amounts of 10-60% of their volume. On the basis of an x-ray diffraction study, the smectite is a dioctahedral variety ($d_{001} = 1.496$ -1.497 Å). The variations observed in the d values of the small angle basal reflection 001 reflect variations in the composition of the exchangeable cations in the mineral structure. The most widespread form of the smectite is a K-Ca-Mg variety with $d(001) = 14.7$ Å. The chemical composition of the fraction <0.001 mm, which contains this form of smectite together with traces of an x-ray amorphous substance (glass) and cristobalite is given in Table 2. Taking into consideration that in the analysis approximately 12% of the SiO_2 belongs to the free silica, the structural formula of the smectite has the form:



In accordance with the classification of the smectites given in [4], this smectite is a high-charge Al-Fe montmorillonite, since it satisfies the conditions: $x \leq 0.2$; $0.2 \leq y \leq 0.5$, and $0.2 \leq z \leq 0.5$, where x is Al(IV), y is R^{2+} , and z is Fe^{3+} .

Hydromica is noted throughout the entire section, but in small amounts. It forms primarily from phlogopite and plagioclase. Its presence is identified in the diffraction diagrams by the series of reflections 00 l with $d(001) = 10.1$ -9.9; 9.8; 9.9 Å, for an air-dried, glycerin-saturated sample calcined at 550°C, which gives grounds for assuming the presence of 5 to 20% swelling interlayers in the structure of the mica mineral.

Leucophyllite is a rare mineral belonging to the group of micas with the theoretical composition $\text{KMgAlSi}_4[\text{O}_{10}(\text{OH})_2]$ that is widely distributed as a pseudomorph of the matrix of conglomerates. In the rock, the leucophyllite appears as cryptocrystalline aggregates of light blue-green color, sometimes with a greasy luster. The monomineralic composition of the

fraction <0.001 mm allowed us to obtain a qualitative powder diffraction diagram of the mineral, as well as diffraction curves from oriented air-dried samples saturated with glycerin and calcined at 550°C (cf. Fig. 4). The mineral is a dioctahedral mica of the 1M polytype with the unit cell parameters $a = 5.207$, $b = 9.018$, and $c = 10.06$ Å; $\beta = 100.56^\circ$. When the sample is saturated with glycerin, displacement of the first basal reflection from 9.8 Å (air-dried sample) to 9.7 Å is noted, which is due to the presence of about 10% swelling of the 2:1 layers in the mineral. The thermal analysis curves for the leucophyllite (cf. Fig. 4) differ from those given in the literature. The endotherms at 85°C and 610°C are somewhat shifted and are very weak. The total weight loss on heating is 6%. A shift in the effects is also observed in the IR spectrum (cf. Fig. 4). This applies in particular to the deep maximum in the region of 3751 cm^{-1} reflecting the stretching vibration of the OH groups.

Recalculating the chemical analysis (cf. Table 2) leads to the following structural formula: $\text{K}_{0.73}\text{Na}_{0.30}(\text{Al}_{1.04}\text{Fe}_{0.30}^{2+}\text{Mg}_{0.62})_{1.96}(\text{Si}_{1.98}\text{Al}_{0.02})_{4.00}[\text{O}_{10}(\text{OH})_2]$. The structure of the mineral is characterized by a negligibly small replacement of Si by Al in the tetrahedra, the presence of a significant amount of Fe^{2+} in the octahedra, and a high Na content in the interlayers.

Calcite replaces up to 90% of the rock previous altered to clinoptilite, and fills small fissures in the tectonically disturbed portions of the section. In some instances it is associated with dolomite.

Cristobalite is generally detected in x-ray diffraction patterns only by the intensity of the 101 reflection with a d value of 4.03–4.04 Å, and in electron micrographs by the characteristic shape of its segregations. It occurs primarily in the lower part of the section in association with clinoptilite II and ferrierite. It fills late fissures, where it takes the form of white, opaque porcellanous segregations with a characteristic conchoidal fracture.

Thus, it is possible to note both similarities and differences in the lithology and mineralogy of the two sites described here. Both sections are composed of interstratified volcanic-sedimentary, sedimentary-volcanic, and sedimentary rocks, but the Tsagan-Tsab section is enriched in sedimentary-volcanic rocks, and in the Tushleg section the greater part is occupied by volcanic-sedimentary types. The most highly reactive rocks of both sections are the vitroclastic tuffites. The major zeolite is a Ca-K clinoptilite. Its content varies (at Tushleg) from 0 to 60%, averaging 25–30% in the tuffites, and from 0 to 80%, averaging 40–60% in the tuffites, (at Tsagan-Tsab). Because of the significant admixture of terrigenous material, the cation composition of the zeolites differs from that of pure clinoptilite. This must be borne in mind when comparing the Mongolian rocks with zeolites from other areas of the world and in making decisions about their practical application. The list of authigenic minerals at Tushleg is significantly longer than at Tsagan-Tsab. The wide distribution of layer silicates in the altered rocks at Tushleg should be emphasized, in particular that of leucophyllite and hydromica, since it is precisely these minerals that are most informative in reconstructing the conditions for post-sedimentational alterations of the original sediments.

PALEOCONDITIONS OF AUTHIGENIC MINERALIZATION AND MINERAL PARAGENESSES

The biochemical methods developed by Ch. M. Kolesnikov for determining the paleocompositions of waters enabled the author [6] to classify the Lower Cretaceous reservoir of Mount Tushleg as chloride-sulfate-sodium-magnesium with mineralization of 6.1–9.7%, i.e., the composition of the water of the paleobasin, according to the data in [6], was close to that of modern seawater. This is confirmed by fossil studies made at the section by D. Khand (oral comm.) of the Geological Institute of the Academy of Sciences of the Mongolian Peoples Republic [GI AS MPR]. On the basis of the visible composition and morphological features of the ostracod shells of Tsagan-Tsab and Shinkhuduk age she concludes that the basin in which the sediments of these sections accumulated was shallow and had a high rate of sediment accumulation and elevated mineralization of the water.

By contrast, the fauna of the Tsagan-Tsab paleobasin were freshwater varieties. In the modern section are found numerous fish fossils, lycoptera of the species *Lycoptera middendorfi*, which inhabit the surface layer of fresh waters [3]. Fossilized insects have been found: (A. G. Ponomarenko of the GI AS MPR, oral commun.) which are almost never found in saline or even slightly saline waters. Accordingly, the mineralization of the paleobasin of Tsagan-

Tsab was slight, amounting to 0.6-1.4%, a value given by Ch. M. Kolesnikov [6] for hydrocarbonate-calcium waters.

Such differences in the composition of the mineralizing medium could not avoid being reflected in the range of species found and the composition of the authigenic minerals, which is what is in fact observed (cf. Fig. 1). While only four new mineral forms are found in the rock section at Tsagan-Tsab that have a composition close to that of the original tuffite, something on the order of a dozen new mineral forms are observed at Tushleg with a chemical composition that does not allow their formation to be considered to have occurred simply as the result of the breakdown of continental rocks. It is chiefly the major authigenic mineral, clinoptilite, that differs in composition (cf. Fig. 5), the samples from Tushleg being characterized by a higher content of Ca (Na + K) than those from Tsagan-Tsab. Differences in composition are also noted for another mineral found throughout the two zeolite sites, the smectite. At Tsagan-Tsab it is the Na-Ca form that is widely disseminated, and at Tushleg, the Ca- and Ca-Mg forms. In the rocks of the Tushleg locality, authigenic hydromica and leucophyllite are widely represented, minerals with a high K content, and Mg zeolites, ferrierite and dolomite are noted, i.e., the cation composition of the authigenic minerals clearly reflects the characteristic features of the mineralizing medium. The interaction of fresh, low mineral-content waters with the tuff leads only to the redistribution of its original components with no change in overall chemical composition. Waters with elevated mineralization do not only dissolve the original volcanic material, but also add their own cation load to the mineralizing medium.

Another important feature of the authigenic minerals is the order of their formation and the mineral parageneses. At Tsagan-Tsab either only one authigenic mineral is observed, the clinoptilite, or the stable mineral paragenesis clinoptilite-smectite, with the zeolite playing the leading role. In fissured sections, cristobalite is added to this paragenesis, which likely crystallizes as a result of the loss of excess silica (from the slight dissolution of quartz and the recrystallization of acidic glass in the clinoptilite) to the open space of the fissures. This kind of authigenic mineralization is evidence that the original rock underwent alteration under the same conditions at different times and in different locations.

At Tushleg more complex parageneses formed: 1) clinoptilite-smectite-hydromica, which persists throughout the entire section; 2) chlorite-smectite-leucophyllite, which is characteristic of alteration of the cement in the conglomerates of the upper part of the section; and 3) clinoptilite II-ferrierite-calcite with cristobalite, which is restricted to late fissures in the lower part of the section.

The first paragenesis develops from the original tuffite on direct contact of the tuffite with the mineralized water of the paleolake. In terms of formation type and position in the section it is completely analogous to the clinoptilite-smectite paragenesis of Tsagan-Tsab, but differs from it in the more extensive development of smectite, hydromica, and the presence of several generations of the same mineral and the presence on the authigenic minerals of signs of dissolution and recrystallization. Accordingly, the formation of this paragenesis proceeded for an extended time, with a relatively high content of Mg and K in the mineralizing solution, the conditions of mineralization changing with time. In particular, the clinoptilite that was stable at the beginning of the process could dissolve and recrystallize or be replaced by minerals more stable under the changed conditions (cf. Fig. 2g).

The chlorite-smectite-leucophyllite paragenesis is observed only in those parts of the section where coarse clastic material is present. The major mineral of the paragenesis, leucophyllite, develops together with smectite from the glass of the tuffite that serves as a cement in the conglomerate or gravelstone. Chlorite (penninite) completely replaces biotite in the tuffite, and the hydromuscovite present in subordinate amounts develops from plagioclase crystal clasts. In nature, leucophyllite is a rather rare mineral. Observations made by different investigators [9, 10] provide evidence that it forms principally during the recrystallization of volcanic glass, either under hydrothermal conditions or by the action of the highly mineralized waters of evaporite basins. T. N. Sokolova et al. [10] give a value for the salinity of the environment in the formation of leucophyllite of 27-32%. In the case of the formation of leucophyllite at Tushleg, the proximity of the volcanic structure and the abundance of ash material are not inconsistent with its being of hydrothermal origin, but the absence of zoning about the fissures, the constant restriction of the paragenesis to coarsely clastic varieties, and its areal extent are more in favor of an evaporitic origin. The conglomerates at Tushleg require further study, but the possibility is not ruled out that they were deposited under low-water, supersaturated conditions in the lake when the parameters of

the water were different from those existing during the accumulation of the sandy siltstones and pelitic rocks of the section. The presence of leucophyllite, and the chlorite and hydro-muscovite paragenetically associated with it, as well as the intense reworking of the cement of the conglomerate, appear to support this position.

The third paragenesis distinguished at Tushleg is clinoptilite II-ferrierite-calcite with late cristobalite. It is encountered in the lower part of the section in tuffites close to the contact with the basalt massif. In the contact zone, the tuff-sedimentary sequence has undergone intense tectonic disruption to a thickness of 15 m and carbonate alteration of up to 90% of its volume. The late fissure generation of clinoptilite and ferrierite formed after replacement of tuffite that had previously been altered to clinoptilite by carbonate as a result of the binding of the components released in this process. Thus, crystallization of ferrierite in the rocks described occurs as a result of a fairly complicated multistage alteration process. The multistage nature is expressed in the sequential change of the mineral assemblages: acidic volcanic glass $\rightarrow$ clinoptilite I + smectite $\rightarrow$ calcite + clinoptilite II + ferrierite. The paragenetic relations in these associations show that their formation is separated in time. Carbonatization of the tuffite here is an essential precondition for the formation of the late ferrierite. An experimental study by E. Cormier and L. Sand [13] on the synthesis of ferrierite established that for a constant $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 10 (close to the value in natural ferrierites), changing the values of $\text{CO}_2/\text{HCO}_3^-$ from 0 to 1 allows ferrierite to form even in pure carbonate systems. Under different conditions, ferrierite forms as a metastable phase, and with the passage of time can alter to an association of mordenite with quartz or quartz with feldspar.

Thus, the paragenesis of authigenic minerals observed in the Tushleg rocks have imprinted in them different paleoconditions of mineral formation. The water of a long-lived paleobasin at certain periods became more highly mineralized, to all appearances, and its acidity and temperature conditions changed. Such changes occurred both within local area as well as throughout the entire basin. The elevated mineralization of the water and the change in the paleoconditions led to polymineralic alteration of the original tuffites of Tushleg and the formation of zeolitoliths impoverished in useful components compared to those of Tsagan-Tsab, where the alteration of analogous rocks proceeded for an extended period under the tranquil conditions of a uniform basin.

MECHANISM OF ZEOLITE FORMATION

Experimental studies show [17] that under conditions similar to those of the paleoconditions of Tsagan-Tsab and Tushleg, acidic glass is unstable and undergoes slow dissolution. The dynamics of this process are reflected in the graph in Fig. 6A, from which it follows that the dissolution is in general caused by the removal of silica from the original glass when the remaining components are very or almost completely immobile. The slow removal of silica in real circumstances of glass aging leads inevitably to the breakdown of its original structure with the rupture of existing and the formation of new bonds stable under the given physico-chemical conditions. It is obvious that if we take into account the hydration of the glass that occurs in parallel with the removal of SiO_2 , this stable mineral formed by recrystallization is a zeolite. In this process, the original chemical composition of the glass may provide the entire chemical composition of the newly formed zeolite.

It should be noted that the trends in the mobility of the components during dissolution of the vitroclastic tuff are similar (cf. Fig. 6B). In this case the yield of cation to the solution is higher than for the dissolution of glass, which under natural conditions may contribute to the crystallization of zeolites in the open spaces from pore solutions.

Photographs taken on an electron scanning microscope show details of the process of natural zeolite formation. In the foreground in Fig. 3A (magnification $\times 2000$) a "horn" of the original glass is clearly distinguishable which in this photograph, and even more under the optical microscope, even at maximum magnification, appears unaltered. With greater resolution this "immutability" does not appear so obvious (cf. Fig. 3b, magnification 5000 diameters), and at a magnification of $\times 20,000$ (cf. Fig. 3c) it is possible to see that glass as such has already practically disappeared. What is seen under the optical microscope as glass proves to be composed entirely of the finest (of the order of 1 μm) crystalline pseudomorphs of the glass, i.e., zeolite formation in this case proceeds directly within the body of the dissolving glass by means of its recrystallization, which proceeds in parallel with dissolution (removal of the silica). The process of dissolution is of course maximally developed

in the boundary zone between the glass and the pore space. Accordingly, the synthesis of zeolites proceeds with special intensity precisely in the outer zones of the dissolving vitroclast as a result of these being the most altered (being converted to a hydrogel), as well as due to the presence of the open space that favors the growth of crystals. In this process the cryptocrystalline types of zeolites that develop directly inside the individual grains of the glass are a kind of poison to the formation of large crystals (cf. Fig. 3e, f).

The combination of the processes of recrystallization, dissolution of glass and zeolite synthesis is seen especially distinctly in the photographs (cf. Fig. 3g, h) of a tuffite horn of glass in which is embedded a sand grain of the sedimentary quartz. Relicts of the glass are distinctly visible in the left part of Fig. 3g. Recrystallization begins inside the glass and gradually, in the direction of its outer surface, the appearance of the newly formed crystals of clinoptilite becomes ever more evident. The best formed crystals are noted at the glass-pore space boundary and around the quartz sand grain. This zeolitic rimming of the sedimentary quartz particles is extremely characteristic of the rocks and is apparently explained by the synthesis of zeolites from the dissolved gel surrounding the quartz which is produced by the incomplete dissolution of the glass. The photograph distinctly shows the connection of the original glass and the zeolite border developing near the quartz that supports this hypothesis. In this same photograph one can note the dissolution and recrystallization to cristobalite of the external zones of the quartz itself.

During the breakdown of the glass, the synthesis of smectite and the hydromica occurs only in the zone bounding the pore space (cf. Fig. 4b and d). These minerals can also form during the breakdown of other tuffite components. The result is that we observe several types of layer silicates in the same sample. For example, in sample 237 from the Tsagan-Tsab section Na- and Ca-Na-smectites are encountered that have different $d(001)$ values, equal, respectively, to 12.5 and 13.9 Å (for air-dried samples).

Thus, the processes of authigenic mineral formation that occur during the breakdown of the original glass in the zeolite localities studied can be illustrated by the diagram shown in Fig. 7. The mechanism of mineral formation shown in the lower right-hand part of the diagram is basically realized at Tushleg.

* * *

The information presented here is evidence that the zeolite localities described in this article can be classified as volcanic-limnic zeolites. They form as the result of the break-

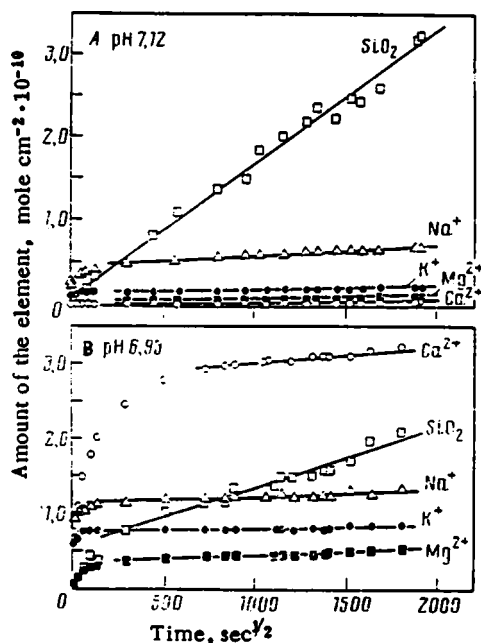


Fig. 6. Experimental data on the growth of acidic glass (A) and crystalline tuff (B) at 25°C from the data of F. White [17].

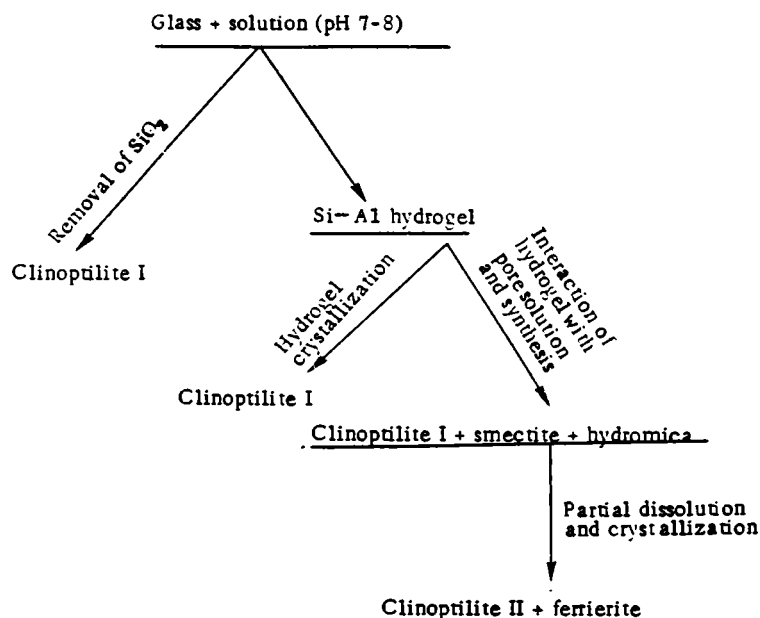


Fig. 7. Scheme of the post-sedimentary alteration of volcanic glass.

down of the volcanic glass of a tuff-sedimentary sequence under the action of neutral fresh and low-salinity waters of isolated paleobasins. The medium in which they formed distinguished them from the well known zeolitoliths of lacustrine origin such as the deposits of a number of lakes in Colorado, California, Nevada, Africa, and some other regions, where the formation of zeolitoliths is a consequence of the interaction of alkaline (pH 8.9-10.1), carbonate (bicarbonate) waters or brines of modern or paleolakes with the acidic (trachytic) glass [14].

The zeolite mineralization in the deposits of salt lakes is fairly specific. The most widespread Na-zeolite is analcime (found at the Green River formation in Colorado, Tulare and Searles Lakes in California, Lake Natron in Tanzania, etc.). It has been observed to crystallize not only in tuff, but in argillite beds as well, in some cases a correlation being noted between the amount of analcime in the sediments and seasonal variations in the chemical composition of the lake water, which serves to a certain degree as evidence of a possible chemical precipitation origin of the analcime. Less widespread, but also characteristic, are erionite and phillipsite (Teels Marsh in Nevada, Lake Owens in California, Magadi in Kenya, etc.). These minerals are encountered exclusively in the tuffaceous parts of the sections, where they replace volcanic glass. An analogous position is occupied by the rarely encountered chabazite and clinoptilite in amounts up to 10% (Lake Natron in Tanzania, Teels Marsh in Nevada, and China and Owens Lakes in California). Very rarely in the deposits of soda lakes natrolite is observed to have developed after nepheline (deposits of Olduvai Gorge in Tanzania).

All of these zeolites are encountered in association with each other, at times in a zonal arrangement. For example, in the Late Pleistocene deposits of Olduvai Gorge in Tanzania, the association of zeolite minerals succeeds each other upward through the section in the following order: phillipsite + erionite → phillipsite + potash feldspar → analcime + chabazite → phillipsite → analcime + chabazite + Fe hydroxides → phillipsite + natrolite. The zoning described here is controlled primarily by the composition of the original rock: phillipsite, erionite, and natrolite are characteristic alteration products of trachytic tuff, and analcime, chabazite, form from aeolian tuff [14].

The dependence of the nature of the authigenic zeolitic mineralization on the nature of the original rocks is also found in the deposits of existing soda lakes. In particular, in tuffs and tuff clays found in the middle part of the Owens and China Lakes sections in California, the major zeolites are phillipsite, clinoptilite, and erionite with distinctly subordinate amounts of analcime, while in the over- and underlying clay (nontuff) sediments of China Lake, the picture is the reverse, and the nontuff sediments of Owens Lake contain practically no sediments. These same lakes and the nearby Searles Lake are evidence that for practically identical pH values (9.1-9.5), different mineral compositions of the water can produce different authigenic mineralization from the same rocks: analcime + phillipsite +

clinoptilite + erionite + searlesite in tuffs altered by the relatively low mineral-content waters of Owen Lake and China Lake, in contrast to the analcime + searlesite + potash feldspar in similar tuffs of the highly mineralized Searles Lake [14].

In addition to the zeolites, other characteristic minerals in soda lake deposits are albite, potash feldspar, quartz, sodium and some boron minerals. In particular instances zoning is observed in their distribution and in the distribution of the zeolites (for example, potash feldspar alternates with analcime in the peripheral parts of the tuff deposits of the Wilkins Peak Member of the Green River Formation in Colorado [14].

According to the data of L. Hay [14], the formation of zeolites in the sediments of soda lakes occurs via their precipitation from solutions enriched in components reproduced by the complete dissolution of the original glass. Zeolitization of the glass in the solid state as it devitrifies or hydrates is not observed. Evidence of this is the formation of zeolites under conditions of free growth, i.e., in pores, vugs, and as a cement forming in open spaces formed by the complete dissolution of the original glass. In the case of the partial dissolution of the glass, its relicts are not altered to zeolite.

In comparison with the classic examples of zeolite lake deposits described above, the zeolitoliths of the MPR display a number of characteristic features.

The major zeolite in them (up to 80 vol. % of the original rock) is clinoptilite, a zeolite not extensively represented in the deposits of soda lakes.

Clinoptilite is developed exclusively in the tuffite parts of the sections, replacing volcanic glass, or more rarely, filling pore spaces; the clastic part of the tuffites is not altered.

The paragenetic associations in which clinoptilite is encountered in the MPR are impoverished and include basically mixed-layer minerals of the smectite-mica type, hydromica, and SiO₂ varieties; sodium minerals and authigenic feldspars are not encountered in the sections described here.

In the zeolite occurrences studied, no spatial zoning was detected in the distribution of the authigenic minerals.

The mechanism by which the zeolites formed varied; primarily this involved the structural rearrangement of the glass components during its slow dissolution, or the crystallization of the zeolites from the hydrogen formed by the hydration of the glass.

The uniqueness of the composition of the mineal-forming environment of the Mongolian paleolakes produced a unique type of volcanic-limnic zeolites. It should be noted, however, that they resemble clinoptilite sequences formed by the diagenetic alteration of glass under marine conditions [15 and others], which is not surprising if one takes into consideration the similarity of the physicochemical parameters of the environments.

Thus, in the MPR large fields of zeolites have been discovered for the first time. Elucidating their origin may help to answer questions about the means by which clinoptilite rocks formed in other regions.

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In the article, we present the results of a modeling of sedimentation on a IGL hydrointegrator. We establish conditions for the onset of a self-oscillating system in a sedimentary basin and show the bottom profile during the stage in which the regime is becoming established and show the development of the regime. Zones where various formations occur are noted and we were able to determine the critical depth of basin necessary for a self-oscillating regime. The influence of initial conditions and external factors on rhythm formation under the conditions of a self-oscillating system are analyzed. In addition, comparisons of data from the modeling with data from natural objects are made.

Geologists have shown an interest in the problems of repetition, cyclicity, and rhythmicity associated with geological processes. The majority of hypotheses attempting to explain the causes of rhythm formation are based upon the assumption that the rhythms reflect a periodicity of external influences upon the geological object. However, there is a point of view that the rhythmicity of geological processes has a self-oscillating character and is connected with the developing geological system itself.

J. R. Beerbower [19] was first to point out that cyclicity in sedimentation can be due to both external (allocyclical) and internal (autocyclical) factors. He believed the causes of the cyclicity associated with alluvial build-up lay in the character of the fluvial environment and the prevailing conditions of transport, sedimentation, and erosion of clastic material. He believed that these influences resulted in channel migration and the formation of sedimentary cycles. His ideas were supported by a series of investigators [4, 6, 15] who assumed that autocyclic sedimentation could be found in other depositional environments but was most characteristic of advancing deltas. Mathematical models suggested by A. V. Luk'yanov [8, 9, 12, 13, and 21] and A. S. Devdariani [1, 5] associated the formation of the rhythmically built-up and genetically interrelated facies of the continental slope with the development of a self-oscillating system in a sedimentary basin.

These models explain many peculiarities in the sedimentary strata and confirm Walther's law (already formulated at the end of the 19th century) that the very formation of sequences of facies is integral to sedimentation and that the facies in the vertical section occur in the same sequence as the sedimentary environments on the earth's surface.

We modeled the sedimentation process in the system on the IGL hydrointegrator system of V. S. Luk'yanov. The possibility of using the IGL hydrointegrator to model a self-oscillating system in a sedimentary basin was theoretically derived by A. V. Luk'yanov [8, 10, 11]. Modeling was used for an investigation of the conditions necessary for the onset of a self-oscillating system and also an analysis of the effect of the initial circumstances and external factors upon rhythm formation under such conditions. During the modeling process, we succeeded in outlining the bottom profile during the stage in which the regime becomes established and during the regime's development. Zones were noted where various formations occur and the critical depth in a basin necessary for a self-oscillating regime was determined.

The Modeling, Basic Parameters of the Model

The conditions associated with problems found to be solvable presume a sufficiently deep basin* with a constant flow of material entering into it from the shore. Transportation

*For the simplicity of the solution, it was assumed that the basin has a limited but sufficiently wide expanse.

of the material along the bottom surface takes place by wave action in the basin and results in random movement of particles in the near-surface layer (the layer of sediment mobility). Below this layer, particles exist in a buried and immobilized state. The transportation of the particles is dependent upon the hydrodynamics of the basin and the properties of the material and is determined by the coefficient of mobility K of the sediment.* We made use of a dependence of the coefficient of mobility upon the depth of the basin $K = f(H)$ during the modeling, based upon the fact that the coefficient of mobility decreases in a nonlinear fashion with depth (the energy level of the depositional environment drops). The nonlinear decrease in the coefficient of mobility with depth is a second important condition associated with the problem. By taking it into account, one can anticipate that the slope of the bottom (the surface of the sediments) should increase with depth for a fixed amount of sedimentation and that the slope of the surface of sediments at a specific depth within any sedimentary basin should reach a critical value at which the incline becomes unstable and begins to slump.

The third condition bearing on the problem stems from the fact that the sediment is partially thixotropic, i.e., its mechanical properties can be altered from shaking to become more mobile. In such cases, not only the surface layers but also significant masses of buried layers should play a role during slumping, and the slope angle should become significantly more gentle than the original following the slump. Values for three critical slope angles are included in the problem: α_1 (or $\alpha_{\max}$), at which slumping begins; α_2 (or $\alpha_{\min}$) at which slumping of even weakly shaken sediment stops; and α_3 , at which movement of the slumping, turbid material discontinues; they characterize the mechanical properties of the sediment in undisturbed, disturbed, and turbid states.

During the course of solving the problem, the modeling showed that the surface of accumulating sediment assumes a slope corresponding to a specific depth, and finally reaches a critical angle (Fig. 1a); after reaching this angle, a lense of sediment is stripped away from the slope. The slope at the foot of this lens equals the second critical angle. The material is transported downward along the slope, most often in the form of a slump or a turbidity flow, and is deposited at the foot of the slope in the form of an extended layer with a surface slope equal to the third critical angle (see Fig. 1b). A constant inflow of material begins to deposit itself on the stripped surface of the first layer's untransported sediments. When the first critical angle is reached, the material again break away, invading sedimentary lenses bounded by the first and second critical angles, etc. (see Fig. 1c, d). Partial scouring occurs simultaneously in the upper portion of layers not buried by the slump of sediments.

The investigation of the conditions for the onset of a self-oscillating system included checking the influence of the initial slope of the basin bottom upon the course of the sediment-deposition process. In a first variant (Fig. 2), we assumed that the second critical angle equaled the initial slope of the bottom $\alpha_1:\alpha_2:\alpha_3 = 8:4:1$; $K = \alpha H^{-2}$ (where α is a proportionality coefficient).

During the first five stages, a thin skin of unworked sediments is deposited and frequent and powerful strippings of slump material occur. Over the course of this period, the depth at which the deposition of reworked material takes place decreases. Finally, the depth of occurrence of the lense of reworked material reaches a level below which sediments formed as a result of random shifting of material do not occur. This limiting depth turns out to be critical for the basin. After the transported sediments reach this depth, uniform deposition of material begins, accompanied by slumping of sediments which have reached the first critical angle over approximately equal time frames.

In a second variant of the problem, we studied the course of sediment deposition on a slope less steep than the second critical angle (Fig. 3). Initially, deposition of a sediment-

*The coefficient of mobility is characterized by the quantity of particles passing through a unit cross-section of a mobile layer during a unit of time at a given point on the basin bottom. The total quantity of particles on a inclined bottom passing through this cross section upward and downward along the slope (corresponding to "plus" and "minus" signs) does not equal zero; it is proportional to the gradient of the bottom surface dx/dH (where H is the elevation of the sedimentary surface on the bottom). Having defined the sedimentary flow q as the total quantity of sedimentary material passing through a unit cross section per unit of time at a given bottom slope, the coefficient of mobility of the sediment can be defined as the ratio of the sedimentary flow to the bottom slope: $K = -q(H/dx)$ [8]. The "minus" sign indicates that the sediment is shifted downward along the slope.

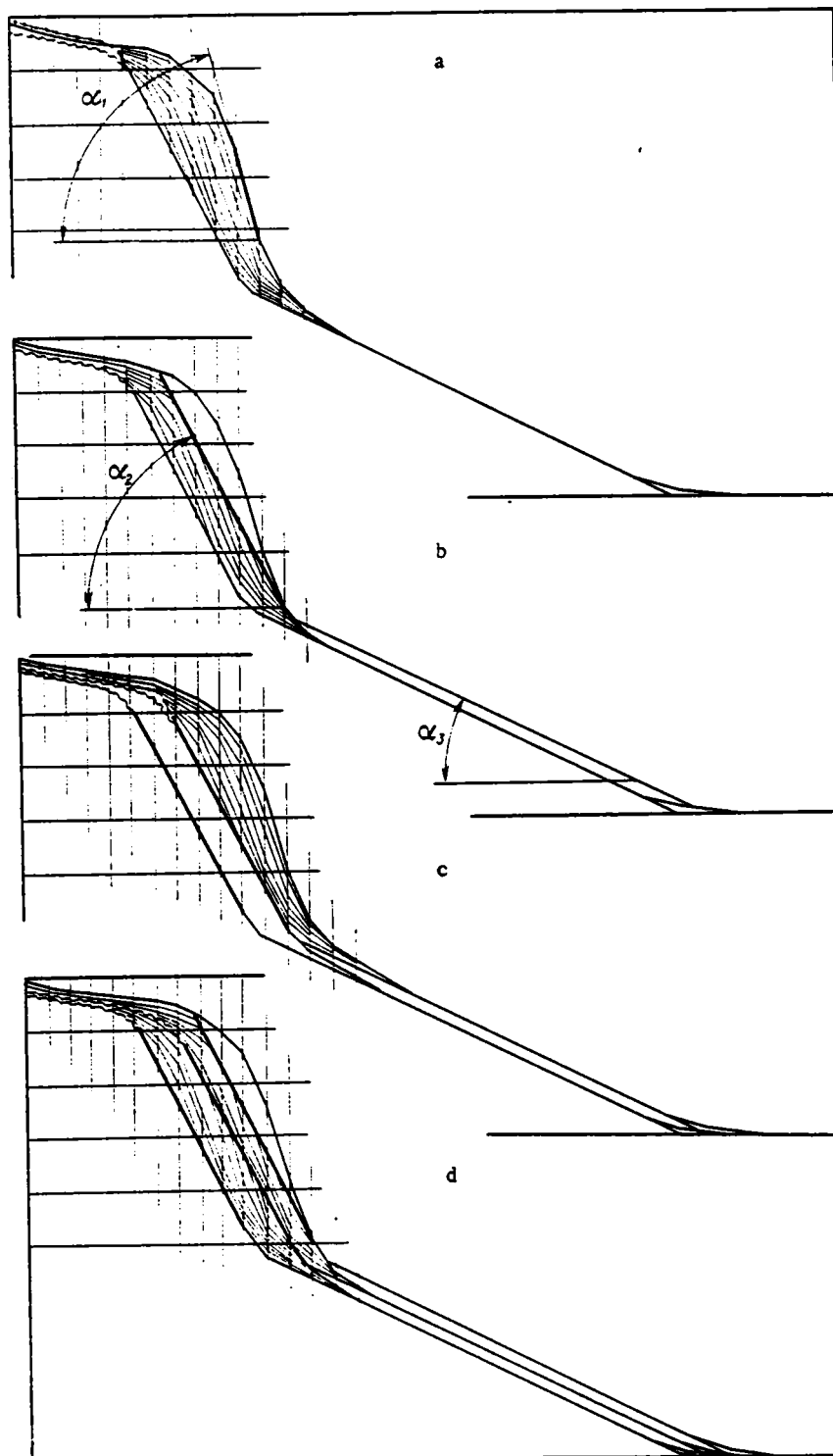


Fig. 1. Formation of rhythmical layering in a basin governed by the properties of a self-oscillating system.

ary lens at the critical depth took place very slowly. However, after the stripping of the initial lens, the sedimentary surface preserved on the bottom of the slope equal to the second critical angle (see Fig. 3a), and the further course of the undertaking proceeding according to the manner of the first variant (see Fig. 3c).

In the third variant of the problem, the initial bottom slope had an angle steeper than the second critical angle, with all of the other conditions of the problem preserved unaltered (the magnitude of the flow, the coefficient of mobility, and the critical angles) (Fig. 4).

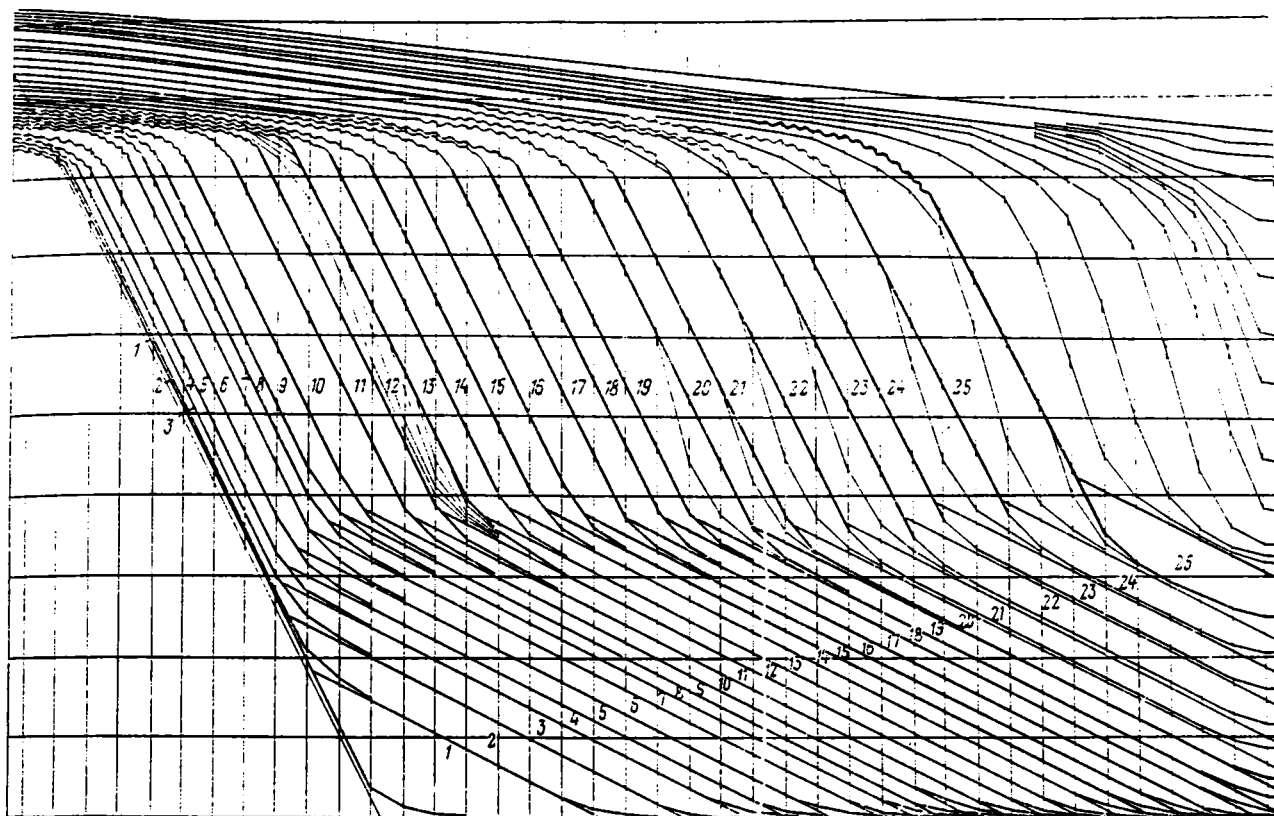


Fig. 2. Progress of basin infilling by rhythmic sediments for an initial bottom slope equal to the second critical angle.

In this case, as in the initial variants, sediments transported by disordered wave action accumulated on the inclined bottom but still, at the beginning, all slid periodically, leaving the initial bottom exposed (see Fig. 4a). Each new lense was stripped away and redeposited, covering the lower-lying lens. Thus, the sedimentary surface gradually rose but did not reach a position where a lens of sediments which has accumulated on a steep slope would not come to rest against a lens of sediments which had slump; the critical depth of the basin was manifest in this manner (see Fig. 4c). After this, the foot of the next slump proceeded over the original bottom and a portion of the sediments came to rest upon it. During the following stage, sediments began to be deposited on a surface inclined at the second critical angle, and the process would develop as it developed during the first variant (see Fig. 4d).

Thus, the rhythmicity of the sediment deposition depends upon the initial conditions only during the first stages of the model's development, when the regime has still not become established. With the emergence of an established regime, the rhythmicity is independent of these conditions and is determined by the properties (parameters) of the sedimentary basin itself evolving as a self-oscillating system. The parameters determining the frequency of the oscillations in the systems are: the intensity of the inflow of sedimentary material to the basin (τ), the coefficient of mobility of the sediment, its dependence upon depth $K = f(H)$, and the maximum (α_1 or $\alpha_{\max}$) and minimum (α_2 or $\alpha_{\min}$) slope angle. Actually, the dependence $K = f(H)$ determines the depth at which the critical angle for the slope ($\alpha_{\max}$) arises in the structure; the difference $\Delta\alpha = \alpha_{\max} - \alpha_{\min}$ determines the degree of thixotropy associated with the sediment, which, in turn, determines the dimensions of the sedimentary lens put in motion during the slumping; the intensity of the inflow of sedimentary material τ determines the time involved for the deposition of this lens, i.e., the oscillatory period.

The modeling which we carried out indicates that the bottom surface of a basin approaches, with increasing sediment deposition, a curve with a shape determined by the dependence of the coefficient of mobility upon depth and also upon the mechanical properties of the sediment and independent of the original bottom relief. The bottom profile of the basin during the stage when the self-oscillating regime is being established has a steplike form acquired regardless

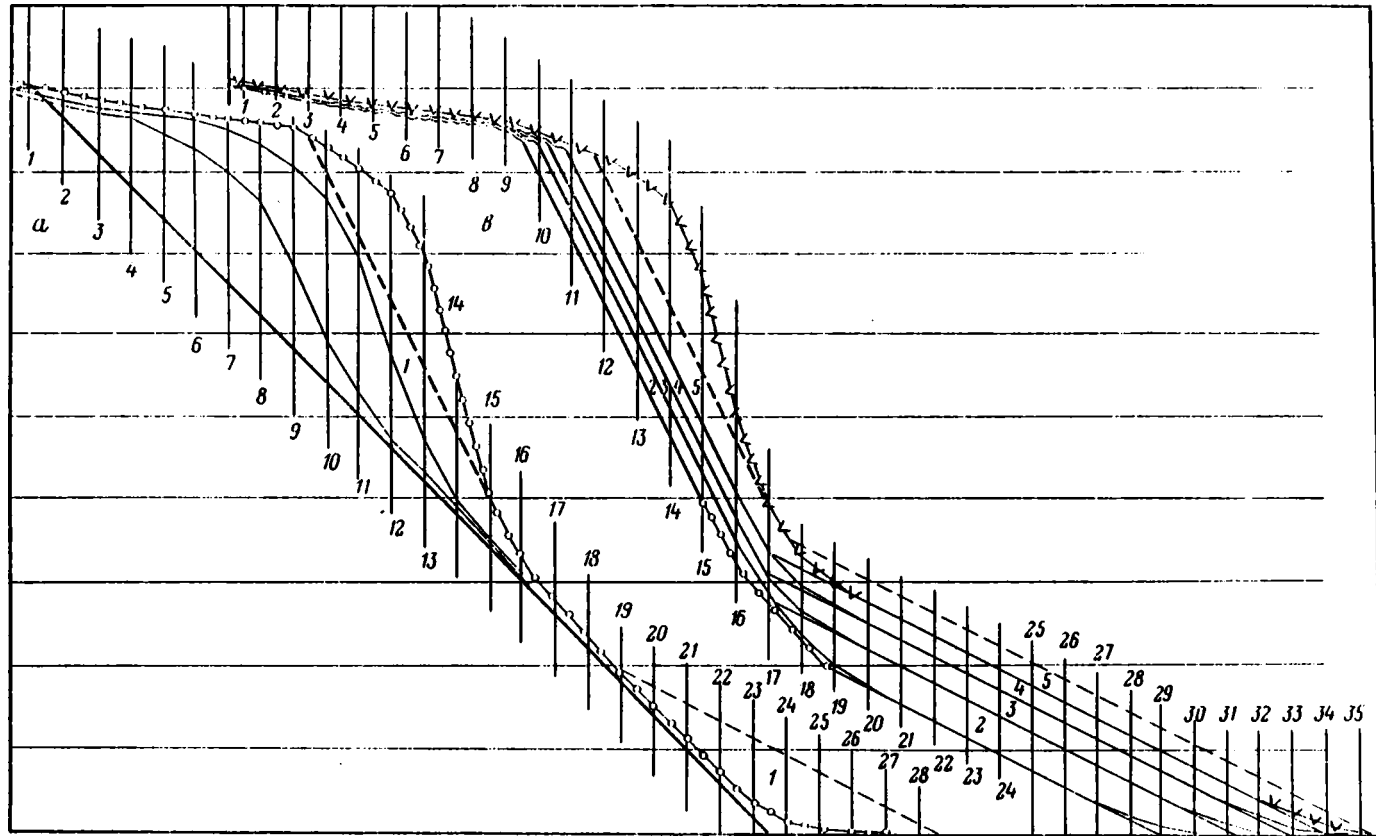


Fig. 3. Progress of basin infilling by sedimentary rhythms for an initial bottom slope less than the second critical angle.

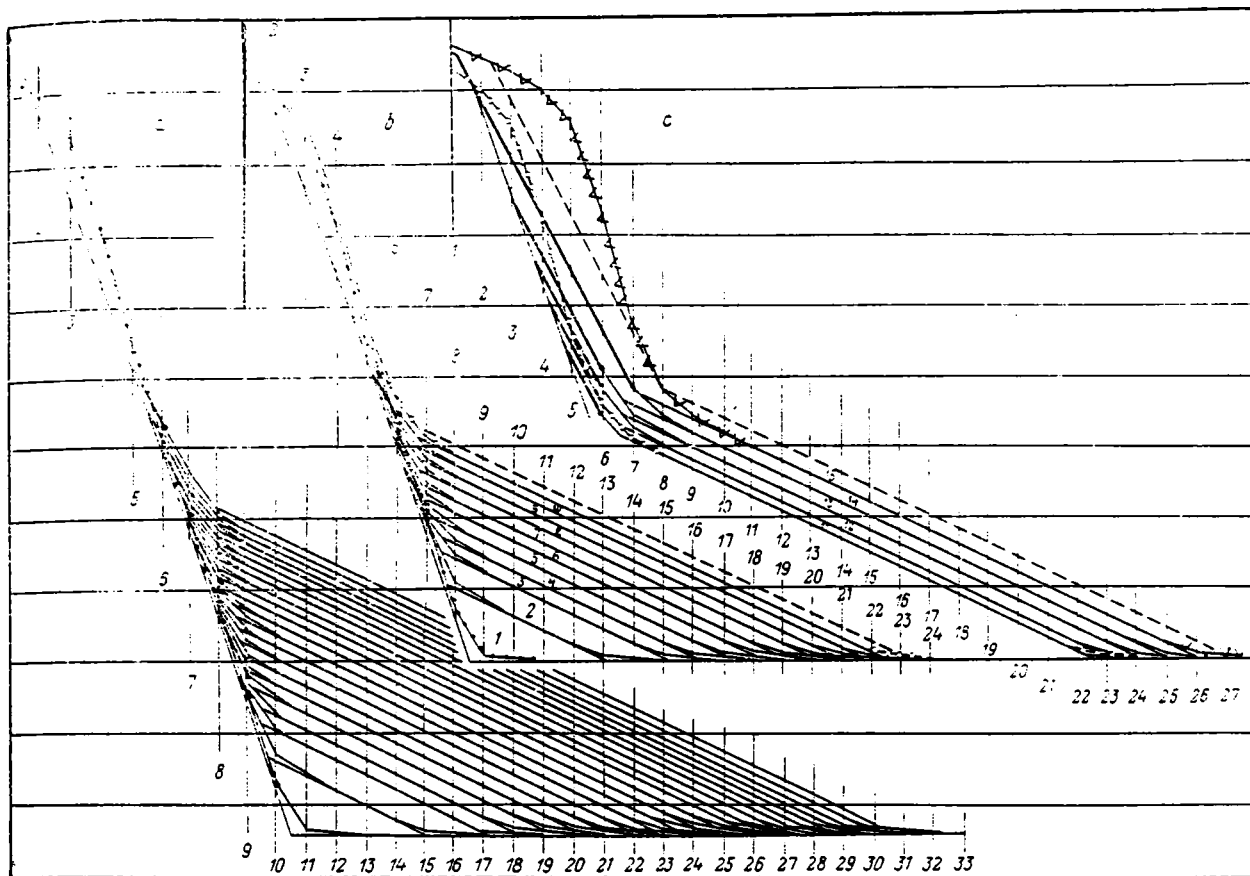


Fig. 4. A pattern of basin infilling by sedimentary rhythms for an initial bottom slope greater than the second critical angle.

of whether the basin boundaries are sharply or gently eroded. Erosion by water takes place as soon as slumping begins on the upper bend of the slope (see Fig. 1 and 2). Material is mainly deposited on a steep portion of a slope constituting a front of sediment deposition. Sediments are deposited on this front rhythmically but in two different manner, depending upon depth.

A critical depth determined by the model's parameters can be clearly delineated within the basin during modeling; this critical depth divides the basin into two zones: precritical and postcritical. The character of sedimentation in these two zones is different for the most part, despite the fact that rhythmicity arises in both zones. Material is transported and accumulated gradually in the precritical zone, but, periodically, some portion of the zone lying at an angle steeper than the second critical angle is removed and undergoes stripping and avalanche transport to the second postcritical zone, where transport and deposition of sediments occurs a bit at a time as a result of periodic arrivals of slides, avalanches, or turbidity flows formed at critical depths. The character of the rhythmic layering is completely different in the two zones delineated. In order to clarify the bedding characteristics of the material during the formation of a single layer or a single rhythm, we took intermediate values determining the position of the sedimentary surface over the course of several steps in the modeling on the IGL until the critical angle of the surface was reached. These intermediate surfaces are also convex curves which cut the plane of the stripping at a high angle (see Figs. 1 and 2). Thus, sediments formed in the precritical zone have nonparallel, stripped, inclined layering. Under the conditions of the problem, we are not able to model the internal structure of individual rhythms in the postcritical zone, but we can assert that it is different here than in the first zone and is most likely parallel or convoluted, as is characteristic of turbid flows.

Thus, with the establishment of a self-oscillating sedimentary regime during the infilling of the basin, a rhythmic layering of rock of underwater landslide or turbidite origin and a rhythmic layering of obliquely laminated rock with truncated or scoured surfaces of

rhythms are simultaneously formed and succeed one another in the form of clinoform lenses. In addition, deposits of the precritical zone always lie above the deposits of the post-critical zone in vertical sections (see Fig. 1) because the front of sediment deposition passes through both zones. Being gradually shifted toward the central parts of the basin, the front of sediment deposition leaves behind a thick layer of sediments, the lower portions of which were formed at postcritical depths and the upper portions of which were formed at precritical depths.

We have discussed above a number of features of the rhythmicity manifest in the model of basin sedimentation resulting from the creation of a self-oscillating system. This rhythmicity and its features owe their existence to the internal characteristics of the basin rather than to external pulses. Thus, we will proceed to a discussion of oscillations in a self-oscillating system. We must now briefly remark upon the relationship between these oscillations themselves and the forced oscillations created in such a system under the influence of external pulses. The investigation showed that these relationships are complex and that each external pulse exerts an effect upon the rhythmicity arising in the system. Correspondingly, megarhythms caused by external effects depend to a significant degree upon the intrinsic oscillations and the external characteristics of the self-oscillating system.

The analysis of the interaction of intrinsic oscillations with external pulses is most simply carried out using the uncomplicated calculations in the simplest model. Let a self-oscillating system in a basin generate intrinsic rhythms with a definite period T_1 and, for example, let the external pulses regularly manifest from earthquakes with a period T_2 . We will assume that alumping of a lens of sediment accumulated in a quiet state occurs at a slope angle α_1 and at a lesser angle α_1' at the moment an external pulse arrives (a tremor caused by an earthquake). Let the angles α_1 and α_1' be given and let $\alpha_2 < \alpha_1' < \alpha_1$. The flow of sedimentary material to the basin can be assumed constant; as a result, the thicknesses of the sedimentary rhythms are proportional to the time taken for their deposition. A lens with a slope angle α_1 is deposited after a time T_1 , and a lens with a slope angle α_1' is deposited after a time T_2' (Fig. 5). We will refer to rhythms formed as a result of the intrinsic oscillations of a self-oscillating system as intrinsic rhythms, rhythms formed under the influence of external pulses will be referred to as extrarhythms, and repeating complexes of several intrinsic rhythms and extrarhythms will be referred to as megarhythms. In the model under discussion, it is easy to show that the duration of the megarhythms T can be determined by the expression $T = n[k + (l/m)]T_1$, where T is the duration of the megarhythms determined by the period of extrarhythm appearances; T_1 is the duration of the intrinsic rhythms; and n , k , l , and m are coefficients expressed by positive whole numbers and characterizing the ratio of the magnitudes of T_2 , T_1 , and T_2' , i.e., the period of the external pulses and the time involved in the deposition of sedimentary lenses with slope angles α_1 and α_1' (see Fig. 5). These ratios can be determined by the expressions:

$$T_2 = [k + (l/m)]T_1; T_2' \leq n(l/m)T_1; l < m.$$

The significances of the coefficients presented are as follows: k and l/m are, respectively, the whole and fractional portions of the quantity T_2/T_1 , n is the number of the external pulse causing the slump and the formation of the extrarhythm, nk is the number of intrinsic rhythms in a megarhythm, $n(l/m)T_1$ is the time for the deposition of an incomplete lens which slides as a result of an external pulse and leads to the deposition of an induced rhythm (an extrarhythm).

In Fig. 5, we have presented an example of a model of the build-up of a rhythmic stratum formed as a result of a superposition of forced oscillations on intrinsic oscillations with the following characteristics: T_1 , T_2 , and T_2' equal to 7, 23, and 5 average time units. The coefficients have the following significance: $k + (l/m) = T_1/T_2 = 23/7$, i.e., $k = 3$, $l = 2$, $m = 7$, and $n = 3$. For these values of the coefficients, the period of the forced oscillations $T = n[k + (l/m)]T_1 = 3[3 + (2/7)]7 = [9 + (6/7)]7 = 69$, i.e., a megarhythm is formed after 69 time units and contains nine intrinsic rhythms and one extrarhythm having a volume equal to $6/7$ of an intrinsic rhythm. During the formation of the megarhythm, two pulses end inconsequently (since the lens of sediments still had a volume insufficient for slumping at the moment of their manifestation) and only the third pulse leads to the formation of the extrarhythm.

It should be noted that the character of the megarhythm can be changes substantially even by small changes in the magnitudes of T_1 , T_2 , and T_2' . Thus, if the frequency of earthquakes increases somewhat in the example presented and T_2 decreases by only two units (T_1 , T_2 ,

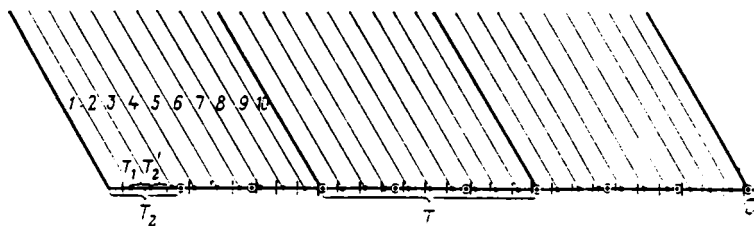


Fig. 5. Progress of the infilling of a basin with rhythmic sediments during the occurrence of tectonic effects.

and T_2' will be characterized by the numbers 7, 21, and 5 respectively), the coefficient ζ goes to zero and extrarhythms do not arise. Of the strength of the earthquakes increase somewhat and T_2' decreases by a unit (T_1 , T_2 , and T_2' will be characterized by the numbers 7, 23, and 4), the duration of the megarrhythm decreases significantly. The coefficients will take on the following values: $k = 3$, $\zeta = 2$, $m = 7$, and $n = 2$. $T = [6 + (4/7)]7 = 46$. Thus, a megarrhythm will be formed after 46 units of time and will contain six intrinsic rhythms and one extrarhythm having a volume equal to $4/7$ of an intrinsic rhythm.

In the examples presented above, we analyzed the simplest model for the superposition of external pulses on the intrinsic oscillations of the system. Even in this simplest case, small variations in the parameters result in substantial changes in the megarrhythms. In order to take into account the conditional nature of periodic earthquakes and earthquakes with different intensities of impact, more complex models leading to the formation of megarrhythms of very complicated character should be considered.

Geological Significance of Conclusions Obtained from Modeling

The steplike bottom profile discovered during the modeling (the steep portion this profile coincided with the main area of sediment deposition) and the gradual advance of the front of sediment deposition toward the central areas of the basin are in good agreement with observations concerning modern sediment deposition on continental margins. Numerous data from seismic profiles and wells have now been obtained indicating that a lateral development of sediments bounded by clinoform surfaces [14, 15] goes on in the region of the continental slope. Sedimentary bodies bounded by clinoform surfaces can extend from deep-water regions to shallow water regions. Rich [23] has delineated three zones within them corresponding to topographic sedimentary environments: fondoform (deep bottom), clinoform (morphological incline) and undofrom (shallows).

Modeling data on the existence of two significantly different zones of sedimentation with genetically distinct rhythms of sediment deposition on the slope and a lateral transition of the zones to nonrhythmical sediments of the shallows and deeps also find their analogs in the vertical variability in the sediments of the continental slope as actually observed.

Marine investigations have established that a sequential deposition of sediments takes places along bedding surfaces initially inclined at angled of $1-5^\circ$. These paleosedimentational surfaces are isochronic. The sedimentary bodies bounded by these surfaces (genetic increments [15]) include sediments of the shelf, deltaic platform, continental slope, delta, and prodelta fronts, and the foot of the continent. The shelf zones are characterized on seismic profiles by unbroken bedding. The facies of the shelf rim show layered, nonlayered, and chaotic patterns. The transition from the shelf zone to the zone of the continental slope can be identified by the replacement of discontinuous, strong reflections (the deltaic-plain facies) by continuously interfingering reflections. Lens-shaped (clinoform) bedding with internally reflecting surfaces obliquely oriented with respect to the grains of the lens are characteristic of the facies of the continental slope. Truncated adjacent deposits are characteristic also. Alteration of interbeds with chaotic and parallel distributions of reflecting surfaces corresponding to deposits of turbidites and hemipelagic muds are characteristic of the central areas of the slopes. The facies of the continental foot, on the other hand, are characterized by parallel patterns of reflecting surfaces. Chaotic patterns connected with the appearance of slumped bodies occur here only at the feet of steep slopes.

Our understanding of critical depth as an important boundary between two types of formations, arrived at which the aid of modeling, allowed us to outline a distribution scheme for

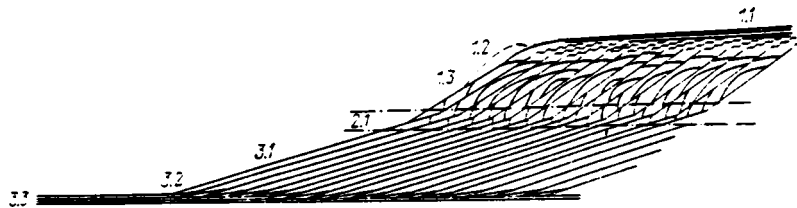


Fig. 6. Distribution of different types of rhythmic sedimentary deposits (facies zonation). See Table 1.

various of sediments in the transition region between the shelf and deep water (Table 1, Fig. 6).

The following patterns were noted during the analysis of the model. Among sediments occurring as clinoforms wedging out at the brow and foot of a slope, four complexes accumulating at different depths can be delineated: 1) nonrhythmic deep sediments; 2) transported sediments at postcritical depths; 3) residual sediments before critical depths; 4) mixed sediments at critical depths. Three subzones can be delineated in the upper complex of rhythmic sediments in the zone of unstable sediment accumulation: transportations, periodic scouring, and periodic strippings characterized by unbroken interstratification, disturbed layering, stripped inclined layering, respectively and probably corresponding to: 1) inner shelf; 2) outer shelf, and brow of the continental slope; 3) upper portion of the continental slope. In the lower complex of rhythmic sediments in the zone of stable sediment accumulation (the lower portion of the continental slope), subzones of episodic inflow of material (series with gradational layering) and deterioration of the effect of slope (series with a playing out of gradational layering) can be delineated. The deep-water deposition complex is characterized by parallel-layered, undisturbed sediments settled out of the water layer and transported by other means than the sediments of the first three complexes.

It follows from the model that rhythmic sediment deposition will continue until there exists in the basin a region with postcritical depths within which clump material from the region of precritical depths can rhythmically segregate. The postcritical depths are a result, in turn, of a rhythmic build-up of sediments in the precritical zone. After the basin is infilled to the critical depth and the depth becomes less than the critical depth, slumping is prevented and a self-oscillating system can come into existence. It is evident in Fig. 2 that the convexity of a curve enclosing a sedimentary surface and not reaching the first critical angle α_1 always decreases and that the surface of sediments being deposited gradually approaches horizontal with the basin becoming completely infilled. The geological outcome following from these data involves a reconstruction of the paleotectonic depositional environment of rhythmically built up strata and also the formational features associated with large-scale sedimentary rhythms in sedimentary series.

According to the model obtained, three stages can be distinguished in the development of sediment deposition and in the formation of the bottom profile of the basin. During the first stage, sediment deposition proceeds only below the critical depth at steepnesses of the bottom exceeding the second critical angle α_2 . The strata of sediments deposited at critical depths consists of rhythmically repeating layers formed by material redeposited in the form of slides or turbidity flows and initially accumulated in the precritical zone. The periodicity in the arrival of this material is determined by the periodicity manifest in the first critical angle α_1 , reached by the sedimentary surface in the precritical zone, a periodicity dependent upon the parameters of the basin. In general, this stratum, composed of rhythmically repeated deposits of turbidity flows, may correspond to flysch, according to suggestions formulated in [22].

Characteristic features of the deposits of the first stage include their transgressive mode of occurrence and also the absence of sediments of the precritical zone; this is in agreement with geological data. The absence of a shelf or its insignificant dimensions is a characteristic feature of flysch basins [2].

M. G. Leonov, having gathered voluminous material from ancient and modern flysch basins, asserts that the flysch in the Black Sea basin is separated from the shelf deposits by a zone in which modern sediments and scouring of more ancient deposits is absent. At the same time, this investigator has brought forward conclusive evidence that the formation of the flysch

TABLE 1. Types of Rhythmical Sediments

Zone	Subzone	Complex	Series
1. Precritical depths (unstable accumulation)	1.1. Transport sediments	Residual sediments	1.1. Continuous interstratification of rock
	1.2. Periodic strippings		1.2. With disturbed bedding as a consequence of periodic scourings
	1.3. Periodic scourings		1.3. With stripped, inclined bedding
2. Critical depths	2.1. Mixed deposit	Mixed sediments	2.1. With complex bedding
3. Postcritical depths (stable accumulation)	3.1. Episodic inflow of material	Shifted sediments	3.1. With gradational layering
	3.3. Lessening of slope influence		3.2. With play out of gradational layering
	3.3. Deep accumulation	Nonrhythmic sediments	3.3. Horizontal bedding

occurs in the zone of the subaqueous slope and at its foot. He rightfully believes that such concepts as the "flysch basin" should be dropped and that one should speak of a zone of flysch formation within a basin where deposition of other types of sediments occurs simultaneously [7].

A stable profile of the basin bottom is formed at the beginning of the second stage; the slope of the bottom reaches the second critical angle α_2 in its steep portion. With the formation of a self-oscillating system, deposition of sediments proceeds within such a basin both in the postcritical and the precritical zones. In the postcritical zone, strata of slump and turbidite origin (similar to flysch) accumulates first, and rhythmically alternating layers of rock with inclined laminations and stripped or scoured bedding surfaces accumulate in the same way in the precritical zone. Individual rhythms synchronous with flysch are more large-scale than the latter here. Sharp incongruities between the internal structures and the surfaces enclosing them are evident in the individual rhythms. This confers a generally lenslike appearance to the stratum. These strata have much in common with marine molasse. During the deposition of marine molasse, manifestations of subsqueous slumping creating a secondary oblique layering often arise [3]. Marine molasse consists of approximately of the same types of rock as flysch: argillites, aleurolites, and sandstones with subordinate amounts of conglomerates and marls; this is in complete agreement with the conclusions from the modeling to the effect that postcritical sediments are a product of the redeposition of precritical sediments. Co-occurrences of molasse and flysch strata of uniform age often accompanied by lateral transitions are widely found in natural basins. Thus, a lateral transition of carbonate-sandy-clayey and coarsely fragmental molasse to carbonate-sandy-argillitic flysch occurs in the deposits of the Lower Permian in the Cis-Ural Trough [17]. Alterations of normal-sedimentary and redeposited rock occur in the transitional region from molasse to flysch, indicating complex facies transitions between these two formations.

Finally, a third stage in the development of the basin arrives after the entire post-critical zone is filled with sediments and the depth of the zone is less than the critical depth. At this stage, the stage of disappearance of the self-oscillating system, formation of the types of rhythmic sediments we are considering (see Table 1) ceases within the basin. The slope of the surface of sediments in the precritical zone does not reach the critical angle and the curve of the relief on the bottom surface gradually becomes less tilted and, finally, becomes almost parallel to the water line. Sediments at shallow depths play an increasingly important role in the make-up of the strata formed during this stage. Autogenic rhythmic complexes arising on other manners as studied by J. R. Beerbower frequently participate in the make-up of the latter.

Thus, during the course of three stages in the evolution of a basin determined only by the basin's internal parameters a transgressive-regressive complex of sediments representing a single sedimentational cycle is deposited within the basin. The replacement of transgressive series by regressive series established over the course of a single sedimentational cycle of development without the interference of external forces is an important geological outcome. In the case of a change in the water level in the basin, it can be easily assumed that repetitions of these cycles may be numerous as a consequence of tectonic movements. This can be seen in strata of Cenozoic deposits in both individual areas of the Alpine belt and over entire regions. In addition, the slope of the newly formed bottom can exceed the value of the critical angle in such a pronounced fashion during tectonic movements that the rhythmic sedimentation described will be interrupted by the formation of avalanches and landslides which function to restore the equilibrium profile of the bottom. During this time, strata with olistostromes, which, as a rule, turn out to coincide with the boundaries of transgressive-regressive series, will accumulate [18].

Natural Basins Developing under Conditions of a Self-Oscillating System

The internal structure of modern sediments can be seen on actual seismoacoustic profiles at the coast of Africa, in the Gulf of Mexico, and in the Bering and Greenland Seas [14, 20, 25] (Fig. 7). Here, above the acoustic basement within the shelf and on the continental slope (the inclination of which is approximately 6° ; the slope can be clearly delineated in the bottom relief), strata of terrigenous sediments with a lens-shaped structure can be delineated. The thicknesses of these lenses increase sharply in the region of the continental slope. The lenses are distributed in imbricate fashion in relative to one another and have erosional outer and inner contacts which truncate their internal layering. In sections of the eastern margin of the Atlantic Ocean, on one of the profiles by the shores of Spitzbergen, it is evident that the outer margin of these lenses has a steeper incline than the remaining portion of the slope; this makes the lenses similar to the sedimentary lenses obtained in the model. These deposits pass into a finally rhythmical turbidite stratum at the foot of the slope. The latter lies along an uneven erosional contact on a slumped stratum of chaotic composition. The authors associate the origin of this stratum with differential movements on the western border of Spitzbergen which intensified during the time of its formation (Miocene) and led to the formation of a system of horsts and grabens. The thickness of the stratum decreases sharply in the direction of the continental slope and the boundaries become almost parallel, fixing the surface of the stripping.

A number of investigators [14, 24] studying the sedimentological features of the Pleistocene sediments in the Gulf of Mexico using seismic methods and drilling have concluded that the sediments on the lower portion of the continental slope have a reworked character. Thus, L. F. Braun and U. L. Fischer [14] believe that deposits of the shelf, slope, or deltaic cones subjected to subaqueous erosion along a system of underwater canyons primarily serve as the source of sedimentary material in the facies at the foot of the continent.

Much data has been obtained on the formation of sedimentary lenses prograding to the bottom of the water area and accreting to the slopes and shelves to basins. According to the data of Ch. D. Stewart and Ch. A. Kaugkheya [14], a displacement of the shelf to the bottom of the water area took place in the Gulf of Mexico over Paleogene-Neogene and Pleistocene times. As a result, deltaic clinoforms deposited on the slope (see Fig. 7a) lie within the shelf under a surface of shelf sediments. Two lens-shaped sedimentary strata can be delineated here within the Pleistocene section. Along the inner portion of the shelf, each of these is composed of a thin band of sandy sediments. On the side of the basin, these bands alternate with extended mud complexes underlying the outer shelf. The sediments of the slope are subjected to various degrees of gradational shifting. The authors connect the occurrence of slides with rapid frontal shelf accretion by sediments; this leads the critical angle being reached, instability of the sediments, and their stripping. Sediments deposited on the upper portion of the slope are displaced in the form of broad masses down along the slope and debris cones which flow into one another are formed in the region of the continental rise. The Mississippi cone is the largest of these. It extends 600 km from the shore and alternates with facies of the abyssal plain. In the upper area, the cone undergoes a transition to the coarse grained terrigenous deposits of the continental slope brought in by rivers. In the central area, the cone develops intricate slump complexes over broad areas bordering the region of the initial sediment concentration. The formation of slumps, in the opinion of the authors, occurs sporadically as a result of the gravitational instability caused by rapid

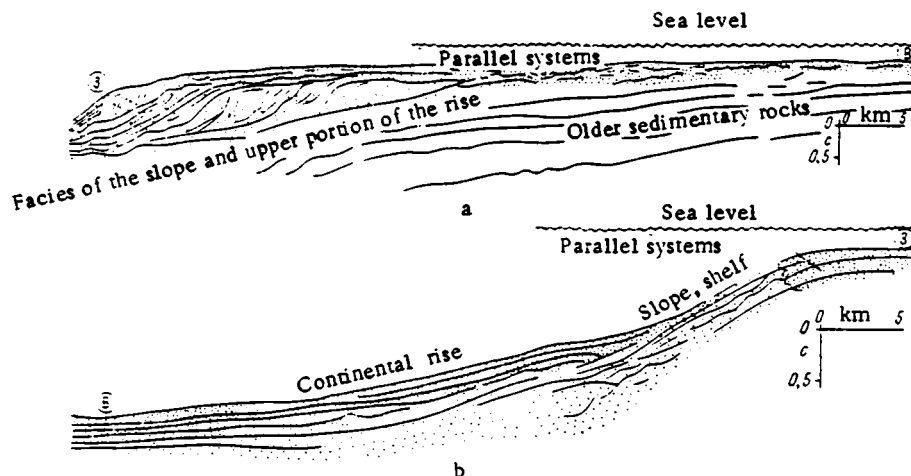


Fig. 7. Diagram of seismic reflections on Holocene continental margins [14] a) reflections characteristic of deltaic and slope systems accumulating on the southwestern coast of Africa; b) deposits of the continental foot at New Scotland.

sedimentation. Chaotic complexes alternate on the seismic profiles with reflecting horizons which are uniform over the area (probably turbidites or pelagic sediments). The lowest portion of the cone is characterized by a small thickness gradient. Uninterrupted reflections are characteristic and, according to well data, deposits of turbidite flows and pelagic muds occur here. On seismic sections, the Pleistocene deposits of the abyssal plain, which the sediments of the lower portion of the debris cone pass into, are mainly represented by parallel-layered types of strong reflections from turbidites and pelagic sediments.

The results obtained during the modeling of a self-oscillating system in a sedimentary basin are in good agreement with data on the forms of modern sedimentary bodies on the continental slopes of these water areas and the manners of their formation. This is evidence for the possible occurrence of self-oscillating systems in natural basins. It follows from the model that the front of sediment deposition advances to the bottom of the basin (see Fig. 2) as a consequence of successive, step-like accretions of sedimentary lenses. In their upper portion, these sediments underlie and give shape to a shallow-water region through which transportation of material takes place, i.e., a shelf. The dimensions of this region are determined to a significant degree by how long the self-oscillating system has been active, i.e., the age of the basin. The geological outcome is that shelves are intrinsic to mature basins and are, at least in the passive-margin region, embanked formations. Actually, if we turn to the International Tectonic Map of Europe made in 1979 [16], we will observe that the broad shelves of the Bering and Baltic Seas and also the eastern coast of Greenland are composed of sediments of Oligocene and Neogene Age and that the young (Oligocene and post-Oligocene) Mediterranean basins are surrounded by thin strips of shelves.

The quantitative evaluation of the process of rhythmic sediment deposition obtained during the modeling makes it possible to proceed to a quantitative evaluation of a natural object using a method similar to that used for our model.

Quantitative characteristics of all the parameters of the model, similarity theory, and the quantitative characteristics of some parameters of natural basins should be investigated for this purpose. Similarity criteria allow us to calculate the remaining characteristics of the process. In this case, the "base model" is a generalized solution providing different interpretations if different base characteristics of the basin are given. All the quantitative characteristics of the model parameters are presented in Table 2 along with three variants in its interpretation: for basins identical with respect to dimensions but differing with respect to the amount of inflow of material, moderate in the first variant and appreciable in the second, and, a variant for shallower basins of smaller dimensions during significant inflows of terrigenous material. The first and second variants simulate the conditions characteristic of the North Sea and the third variant simulates the conditions for the southern portion of the Caspian Sea. The similarity criteria for the model under consideration has the following form:

TABLE 2. Examples in the Interpretation of the Cyclical Sediment Deposition Model

Characteristic	H, m	$q, 10^2$ m ² /yr	α_1	α_2	α_3	$\lg \alpha_1$	$\lg \alpha_2$	$\lg \alpha_3$	$l, 10^3$ m	K, m ² /yr	$\tau_{19},$ 10 ⁵ yrs
Base model	0.53	131	22	11	3	0.4	0.2	0.05	0.008	1.000+100.000	1.9·10 ⁻¹⁰
I	1650	0.08	8	4	1	0.14	0.07	0.02	68.6	0.7+70	21
II	1650	0.07	8	4	1	0.14	0.07	0.02	68.6	1.03+103	9
III	550	0.07	8	4	1	0.14	0.07	0.02	22.8	1.03+103	1

Explanation. H) depth of the model; q) specific flow of sedimentary material; α_1 , α_2 and α_3) critical angles; l) length of the model; K) coefficient of mobility (increases from the lower portion of the model to the upper portion, is inversely proportional to the square of the depth by a factor of 100). τ_{19}) time for deposition of 19 cycles; I-III) interpretation of the model applied to natural objects.

$$\frac{\tau}{l^2 R}; \frac{H}{R l q}; \frac{H}{l \lg \alpha}.$$

If a model is constructed analogous to the one described but with a significant increase in the depth of the postcritical zone, then the thickness of the cycles in this zone decreases in inverse proportion to the depth of the postcritical zone. The time for deposition of the cycles decreases in this case, but not significantly (the order of magnitude remains the same). Thus, the model presented can characterize a sedimentary basin over a wide range of natural conditions.

* * *

The data presented indicates that rhythmic build-up of sedimentary strata can be a result of various causes and that such a build-up is by no means necessarily due to the effects of periodic external forces upon the sedimentary basin. In other words, the rhythmicity of sediments is not of allogenic origin, but is a result of the internal properties of the basin in most cases. It is these properties, in particular, which make possible a self-oscillating system. External influences can undoubtedly disturb the period of intrinsic oscillations in the system and even cause induced oscillations, but they are definitely not indispensable.

The results of the modeling allow us to formulate conditions for the onset of intrinsic oscillations during sediment deposition. The sedimentary basin develops as a self-oscillating system in cases when the following three conditions are fulfilled: 1) the sediments being deposited are thixotropic; 2) the coefficient of mobility of the sediment varies with depth and is a nonlinear function of depth; 3) the depth of the basin exceeds the critical depth, a depth below which entry of material by random fluctuations of particles is practically impossible. These conditions are apparently satisfied in the majority of sufficiently deep basins.

The rhythmicity of sediment deposition in a basin is governed by the properties of the self-oscillating system determined by the system's parameters. The parameters determining the frequency of oscillation in a self-oscillating system are: the coefficient of mobility of the sediment, the pattern of its changes with depth, the intensity of the inflow of sedimentary material to the basin, and the three-critical angles characterizing the mechanical properties of the sediment in undisturbed, disturbed, and turbid states. The parameters enumerated depend, in the first place, upon the peculiarities of the sedimentary material and, in the second place, upon the hydrodynamic regime of the basin. They apparently vary over a significant range in different basins.

The bottom profile of the basin modeled during the stage when the basin's developmental regime was being established has a completely defined, steplike shape and is dependent upon the parameters enumerated above rather than on the initial conditions of the basin. In a sufficiently deep basin, such a profile can become established regardless of whether the boundaries of the basin are initially steep or characterized by the gradual, smooth dip of the bottom.

During the modeling, one can clearly distinguish a critical depth which divides the basin (with respect to depth) into two zones: a precritical zone and a postcritical zone. The

critical depth is determined by the parameters of the system which we have enumerated. Sedimentation in the precritical and sedimentation in the postcritical zones are distinct for the most part, despite the fact that rhythmicity arises in both zones. The deposits of the precritical zone are probably lower molasse; the deposits of the postcritical are probably flysch.

Both varieties of rhythmically built-up sediments are formed over the course of a single stage of sedimentation; they are formed simultaneously and replace one another along course. Moreover, the deposits of the precritical zone always lie above deposits of the postcritical zone in actual vertical sections. Rhythmic sediment deposition continues until the central area of the basin has a postcritical depth and, consequently, both zones are present within it. During the postcritical stage in the infilling of the basin, the depth of the basin becomes less than the critical depth, a self-oscillating system comes into being, and rhythmic sediment deposition comes to a halt in the basin. It can be renewed under the influence of external forces.

The forward-moving front of sediment deposition not only leaves a thick stratum of sediment behind it, but also a relatively shallow-water, flat zone of transported material, i.e., a shelf which is an embanked formation in the case under consideration (involving continental margins).

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A combination of instrumental and chemical methods has been used to detect for the first time in natural sediments — Neoeuxinian sediments of the Black Sea — the presence of sulfide compounds of ferric iron and to characterize their composition. A geochemical mechanism is suggested to explain the formation of these phases, and their importance for reconstruction of sedimentation and diagenesis settings is shown.

Sulfide compounds of Fe(III), except for greigite, had not been found reliably in marine sediments until now, although the theoretical and experimental possibilities of their formation had been discussed on many occasions [1, 5, 6, 12]. Their presence in Neoeuxinian Black Sea sediments has been established by us by means of an x-ray phase investigation of preparations made according to a special method from samples of sulfide hydrotroilite layers collected during leg 8 of the *Vityaz'* Research Vessel in 1984. Samples from sedimentary columns were collected from onboard the ship with maximum precautions to prevent oxidation of the sulfide component of the sediment. Moist ooze containing disseminated sulfides and semisolid lumps were rinsed in anoxic conditions with acetone, sealed, and stored in an inert atmosphere (Ar) in a cooled state. Before instrumental and chemical analysis, acetone was removed by alcohol rinsing, and the sample was dried to powder in an argon current at room temperature. From the experience of laboratory synthesis these conditions are known to limit the possibility of oxidation and intraphase transformations in labile systems and can in fact be conducive to partial crystallization of amorphous phases, allowing x-ray powder pattern diagnosis of chemically separate compounds [3, 4].

The preparation made from sediment of western continental slope of the sea (site 805, coordinates 42°28.1' N lat., 28°51.4' E long., sea depth 1585 m, horizon 362-370 cm from the seafloor surface) appears as a black fine powder with distinct magnetic properties (Fig. 1). The sulfide components oxidize in the air rapidly (5-6 h; in moist conditions 1 h) and dissolve instantly in diluted acids, releasing H₂S and S°, and in hot concentrated alkali NaOH ~ 20%; a red-orange solution is formed which, after staying, becomes decolorized and precipitates iron hydroxide. An ammonia solution of zinc hydroxide (the Stokes reagent [3]) at 25°C virtually does not disintegrate the sulfide.

A highly disperse crystalline sulfide phase has been discovered in this preparation in association with quartz, calcite, plagioclase, and dolomite and chlorite traces. The set of values of spacings and relative intensities of reflection identified it reliably as tetragonal sulfide Fe₂S₃, previously known only from in vitro synthesis [9]. The presence of Fe(III) in a sulfide form was further confirmed by NGR and phase chemical analysis.

The synthetic analog of the crystalline sulfide discovered had been obtained by acting with H₂S on a solution of methylate or ethylate of Fe(III) in an alcohol-benzol mix. The same sulfide, although in a poorly crystallized state, was obtained from an ammonia tartar solution; when H₂S was caused to react with freshly precipitated iron hydroxide, amorphous products were usually obtained. It can be logically assumed, therefore, that the initial precipitate might not have actually contained a crystalline phase which was formed by dehydration of amorphous sulfide during acetone rinsing and drying. Yet, the identification of the crystalline structures of the synthetic sulfide and the one discovered by us, Fe₂S₃, is the necessary and sufficient proof of the presence in the sediment of Fe(III) sulfide, while the degree of its crystallization is of a secondary significance. To this end, from the parameter values of tetragonal unit cell a_0 and c_0 reported in [9], Aleksandrov (All-Union Institute of Mineral Resources) calculated on an SM-1 computer the indexes of all reflections of

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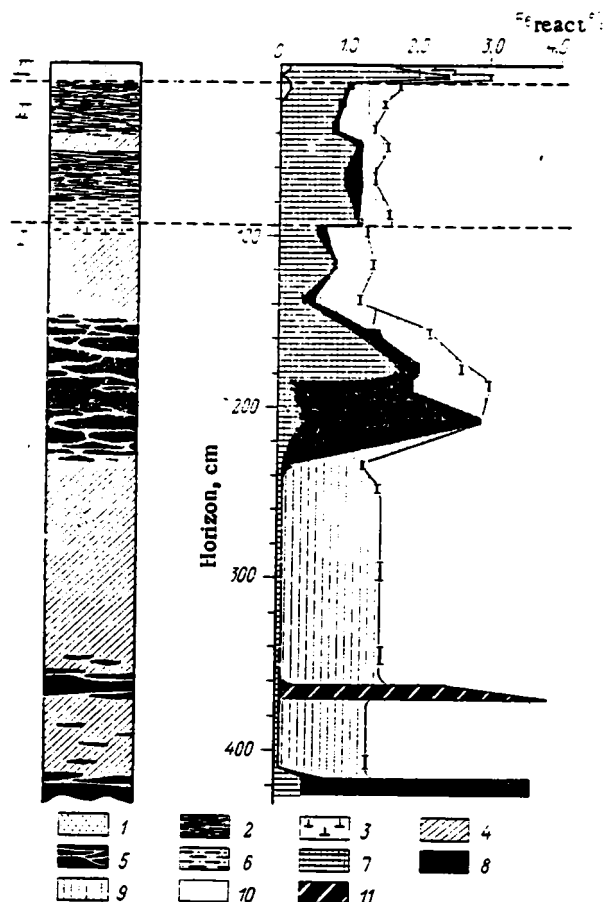


Fig. 1. Lithological characteristics and distribution of the forms of reactive iron (a percentage of carbonate-free matter in sediments) of the western continental slope (station 805, sea depth 1585 m, coordinates 42°28.1' N. lat., 28°51.4' E long): (I-III) horizons (I - Neoeuxinian; II - ancient Black Sea; III - Recent); (1-6) sediments (1 - calcareous coccolithic; 2 - sapropel carbonate-free; 3 - chemogenic carbonate; 4 - terrigenous low carbonate; 5 - same, enriched in dispersed iron sulfide-hydrotroilite; 6 - striated silt-pelitic-transient horizon); (7-11) iron forms (7 - pyritic; 8 - sulfidic Fe(II); 9 - nonsulfidic Fe(II); 10 - Fe(III); 11 - sulfidic Fe(III)).

x-ray powder pattern of the synthetic sulfide, which allowed refining of the parameters of the unit cell and defining the structural characteristics of the phase discovered in the sediment (Table 1).

Studies of preparations by the NGR method revealed three-iron-containing phases. The spectrum is a superposition of a sextuplet corresponding to greigite and two doublets. The doublet with isomeric shift $\delta = 1.25$ mm/sec and quadruple splitting $\Delta = 2.4$ mm/sec from Fe^{2+} ions in a nonsulfide environment is identical to the chlorite spectrum. The second doublet, with parameters $\delta = 40$ mm/sec and $\Delta = 0.55$ mm/sec, characterizes the phases of Fe(III) sulfide. These values correspond to the high-spin state of Fe(III) in octahedral coordination with a high degree of covalence of the bonds. The doublet nature of the spectrum at 300 and 87°K is an indication of a paramagnetic state of the mineral, i.e., the ferromagnetic properties of the preparation generally should be attributed entirely to the greigite admixture. We did not succeed in separating greigite from sulfide by magnetic separation, indicating that the two phases are closely interpenetrated, maybe as a result of a genetic relationship. The existence of such a relationship was confirmed by a second analysis of the specimen with NGR after a 3-month stay at room temperature (and also after a single contact with air), which recorded a decay of Fe(III) sulfide phase with the formation of greigite and nonsulfidic Fe(II).

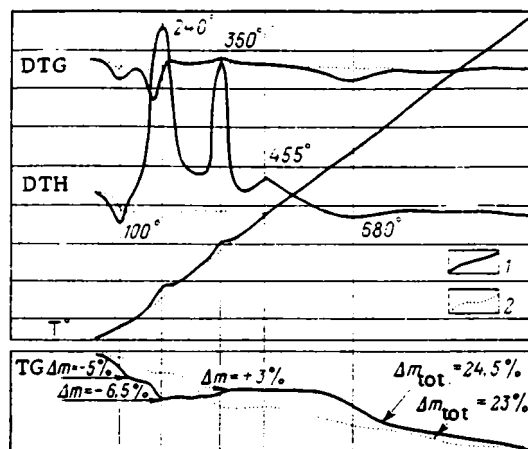


Fig. 2. Results of thermogravimetric investigation of a preparation: (1) in air; (2) in helium (Δm = weight change).

A thermal analysis of the preparation was conducted by Yudin (All-Union Institute of Mineral Resources) on a derivatograph made by MOM using 200 mg aliquots in the air and in a helium atmosphere (Fig. 2). Three exoeffects were registered in the former case: at 240, 360, and 455°C. The reaction at 240°C involved a loss of weight; at 360°C an increase of weight; after 455°C a gradual removal of decay products was observed. The end product (at heating to 1000°C) was hematite. According to x-ray phase control, the intermediate products obtained by heating at 300 and 420°C showed no traits of crystalline sulfide and oxide phases in diffractograms. Oxidative disintegration of Fe(III) sulfide thus occurs as a complicated sequence of processes consisting at a minimum of three stages, with the first two stages corresponding to the formation and transformation of amorphous products. The heating in a helium atmosphere revealed three very weak endoeffects (at 230, 470, and 680°C); a weight loss occurred rather uniformly throughout the temperature interval but was most noticeable at 230°C. The heating to 1000°C yielded magnetite and hexagonal pyrrhotite.

A chemical analysis of the composition of the preparation was difficult because of the presence besides the Fe(III) sulfide of various iron and sulfur compounds that could belong to the original sedimentary material or be products of interphase redox processes in the system $S^{2-} - S^0$. Besides substantial amounts of nonsulfidic Fe(II) and greigite, whose contents according to NGR data increased in a proportion of Fe(II):Fe_{gr} = 1:1 upon decay of Fe(III) sulfide, the preparation can include impurities: Fe(III) of weakly crystallized hydroxide forms and hydromica, amorphous monosulfide, pyrite, elemental sulfur, and also sulfur of sulfates. In view of this, the authors adopted the following sequence of chemical investigation, which required maintaining at each step strictly anoxic conditions (Ar).

After extracting S^0 by acetone and washing with alcohol, pH was gradually lowered by a water suspension of sulfuric acid preparation from 7.5 to 1.0, with intense stirring at room temperature until H_2S was no longer released. This regime provides for complete reduction of Fe(III) in the light-soluble portion of the preparation according to the reaction $2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S^0$. By familiar methods [2, 7] the decay products S^{2-} , S^0 , SSO_4 , Fe^{2+} , Fe^{3+} were determined. A separate weighed amount of the specimen was processed with H_3PO_4 (1:4) to determine nonsulfidic Fe(III), which according to our studies [3], unlike Fe(III) bonded to S^{2-} , forms at 25°C a phosphat complex which prevents its reduction by H_2S being released. The residue that is not dissolved is then decomposed with 1.5 N HCl while heating to 90-100°C; the above products are identified. The preparation was then boiled with $CrCl_2$ and pyrite sulfur was isolated and identified. The results of determinations together with the NGR data characterizing the various stages of decay of the phase of Fe(III) sulfide compound, are given in Table 2.

The intraphase changes that were observed could be due to various causes: periodic stays at room temperature, brief contacts with the atmosphere, and acetone treatment of the sediment. The mechanisms of these factors and the degree of their influence on the change of the composition are to be clarified in the future, as they are highly informative as to the chemical nature of the substances. Interpretations of the results can be based on the following assumptions.

TABLE 1. X-Ray Data on Synthetic and Natural Fe(III) Sulfides

Synthetic [9]			Natural	
<i>hkl</i>	<i>d</i>	<i>I</i>	<i>d</i>	<i>I</i>
021	5.20	10	5.20	10
013	4.12	2	—	—
023	3.49	2	3.48	5
032	3.25	2	—	—
223	2.98	8	2.95	10
040	2.82	1	—	—
015	2.568	1	—	—
332	2.458	7	2.45	7
125	2.334	2	2.35	2
440	1.992	2	—	—
060	1.885	3	1.89	4
154	1.837	6	1.840	3
046	1.733	9	1.735	9
018	1.622	1	—	—
460	1.566	2	—	—
<i>a</i> = 11.30 Å <i>c</i> = 13.05 Å			<i>a</i> = 11.30 Å <i>c</i> = 13.14 Å	

The discovery of individual crystalline structure corresponding to a composition of Fe_2S_3 , determined experimentally [9] (see Table 1) is direct evidence of the presence of a phase with a stoichiometry similar to the above-mentioned one in the preparation. The sulfidization of the amorphous iron hydroxide in an environment of low concentration of sulfidic sulfur (H_2S , HS^- , S^{2-}), however, may lead to the formation of hydroxothio complexes of Fe(III) with a lower sulfur content, which, in terms of coordination chemistry, corresponds to the existence of polymer chains and aggregates of the composition of $\text{Fe}_n^{3+}\text{S}_m^{2-}(\text{OH})_k$. The theoretical composition of greigite is described by the formula of inverted thiospinel: $\text{Fe}^{2+}\text{Fe}_2^{3+}\text{S}_4^{2-}$. The presence of groups of different-valence iron responsible for the ferromagnetic properties and the type of NGR spectrum is beyond doubt [10], but the chemical nature of this sulfide and the genetic relationship with Fe(III) sulfide discovered by us admit broad variations of the composition, especially in the contents of sulfidic sulfur ($\text{S}^{2-}/\text{Fe}_{\text{tot}}$) and possibly in the ratio $\text{Fe}^{2+}/\text{Fe}^{3+}$. It is logical to assume also the existence in greigite of a certain amount of S^0 , which, as well as Fe(II), is a product of a redox reaction in the phase of Fe(III) sulfide and can partially replace sulfidic sulfur in the greigite lattice being formed. The uncertainty as to the composition of the two sulfides makes it necessary to express the sulfidic part of the preparation in variable coefficients:

$$a\text{Fe}^{3+}\text{S}_x^{2-} \cdot b\text{Fe}_{0.33}^{2+}\text{Fe}_{0.67}^{3+}\text{S}_y^{2-} \cdot c\text{Fe}^{2+} \cdot d\text{Fe}_{\text{ini}}^{2+} \cdot 0.13\text{Fe}_{\text{nonsulf}}^{3+} \cdot 0.145\text{S}^0 \times 0.007\text{FeS}_2 \cdot 0.075\text{S}_{\text{so}}, \quad (1)$$

where $a\text{Fe}^{3+}\text{S}_x^{2-}$ is the phase of sulfidic compound of Fe(III); $b\text{Fe}_{0.33}^{2+}\text{Fe}_{0.67}^{3+}\text{S}_y^{2-}$ is the greigite phase; $c\text{Fe}^{2+}$ is nonsulfidic Fe(II) isolated together with greigite and S^0 at the decay of Fe(III) sulfide phase; and $d\text{Fe}_{\text{initial}}^{2+}$ is the nonsulfidic Fe(II) in the initial material (chlorite).

Calculations of the coefficients (under the condition of $\text{Fe}^{2+}/\text{Fe}^{3+} = 0.5$ and absence of S^0 in greigite) yields the interval of possible contents of stoichiometric sulfide Fe_2S_3 , from 0.11 to 0.21 at% in iron depending on the greigite composition:

$$0.21\text{Fe}^{2+}\text{S}_{1.21}^{2-} \cdot 0.32\text{FeS}_{1.33} \quad (2)$$

for greigite composition Fe_3S_4 ($y = 1.33$) or

$$0.21\text{Fe}^{2+}\text{S}_{1.50}^{2-} \cdot 0.32\text{FeS}_{1.16} \quad (3)$$

as calculated relative to stoichiometric sulfide Fe_2S_3 ($x = 1.50$) and its representation in the former case by the formula

$$0.21\text{FeS}_{1.21} = 0.11\text{FeS}_{1.50} + 0.1\text{FeS}(\text{OH}). \quad (4)$$

In the preparation subjected to chemical analysis, at least 10% of iron is in the phase of crystalline sulfide Fe_2S_3 , detected by x-ray investigation. The calculations were performed under the assumption that a minor amount of pyrite (0.007 atomic units of FeS_2), and a possible impurity of monosulfide FeS can be disregarded because the NGR spectrum showed absence of Fe(II) in the specimen in a sulfidic form in a quantitative evaluation of the spectral data with an accuracy of up to 1% Fe (or 0.01 atomic units). The experiment also showed that greigite be-

TABLE 2. Results of Analysis and Compositions of the Specimens

Mossbauer spectroscopy (NGR)				
Analysis number	Time and conditions of stay	% of $\sum \text{Fe}$		
		Fe(III) sulfide	Fe greigite	Fe(II) chlorite
I	4 months after collecting the sample, 5°C, argon	82	7	11
II	3 months following analysis I, 25°C, a single exposure to air	56	21	23

Chemical analysis (8 months after sampling)

Form of the element regime	Oxygen treatment regime		
	$t = 25^\circ \text{C}$		$t = 90-100^\circ \text{C}$
	HCl, pH = 1.0	H ₃ PO ₄ (1:4)	1,5 N HCl
S ²⁻	0,360	0,420	0,082
S ⁰	0,230	0,170	0,014
S ₂ O ₃	0,060	—	0,015
Fe(II)	0,890	0,760	0,033
Fe(III)	Not found	0,130	0,067

III Boiling with CrCl₂ $S_{\text{pyrite}} = 0,014; Fe_{\text{pyrite}} = 0,007$

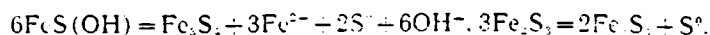
Gross content (decomposition Br ₂ + NHO ₃)	$FeS_{0,920}$
Gross content in the sum of the forms (without S ⁰ initial)	$FeS_{0,775}$
Extracted by acetone S ⁰ initial	0,145

Compositions of the sulfidic portion of the specimen for the theoretical composition of greigite and a content of 0.13 atomic units of nonsulfidic Fe(III)

I	$[0,69Fe^{3+}S_{1,08}^{2-} \text{ or } 0,11FeS_{1,50} + 0,58FeS(OH)] + 0,07FeS_{1,33}$
II	$[0,43Fe^{3+}S_{1,10}^{2-} \text{ or } 0,086FeS_{1,50} + 0,344FeS(OH)] + 0,21FeS_{1,33}$
III	$[0,21Fe^{3+}S_{1,24}^{2-} \text{ or } 0,11FeS_{1,50} + 0,10FeS(OH)] + 0,32FeS_{1,33}$

comes dissolved at room temperature, although slowly. Because of the uncertainty of composition, the nature of this dissolution is not quite clear, but for calculations it can be represented as resulting from two conjugate processes: dissolution of Fe(II) salt of sulfoferrous acid with release of Fe_{sol}^{2+} and H₂S and redox decomposition of acid residue $Fe^{3+}S_m^{2-}$ ($2Fe^{3+} + S^{2-} \rightarrow 2Fe^{2+} + S^0$).

Based on the results of chemical analysis and the above theory, it seems possible to reconstruct the phase compositions of the preparations corresponding to iron distribution as determined by two NGR investigations (see Table 2). These calculations are based on balance of gross contents of Fe and S ($FeS_{0,92}$) and redox decomposition reaction $Fe(II) = 0.5 S^0$; the assumption is that the contents of sulfur of sulfates, pyrites, and nonsulfidic Fe(III) remained constant during the disintegration of the specimen. The nonsulfidic Fe(III) discovered by chemical analysis (0.13 atomic units) must be a part of Fe(III) diagnosed by NGR as sulfidic. Otherwise, the presence of stoichiometric Fe_2S_3 is ruled out because the ratio in the phase of sulfide $Fe(III):S^{2-}/Fe^{3+} < 1$. In view of this contradiction, it should be considered that high lability of the chemical nature of hydrated coordination polymer aggregates of $Fe^{3+}S_m^{2-}(OH)_k$ allows the possibility of formation of fragments of crystalline structure of Fe_2S_3 in a mass of amorphous sulfide as a result of S^{2-} redistribution (for initial $S/Fe \leq 1$) would be isolation of Fe(III) in a highly scattered hydroxide form. It is thus probable that in a real sediment, amorphous or slightly crystallized Fe(III) hydroxy-sulfide could be present with S/Fe close to 1; the preparatory operations described above could be recommended as a technique for detecting such phases by x-ray phase investigation. The calculations for the preparation containing Fe_2S_3 in a crystallized form and a free iron hydroxide show (Table 2) that intraphase disintegration is experienced mainly by the amorphous, more reactive component of Fe(II) sulfide of a polymer type: $[FeS(OH)]_n$. The process of this decay for each of these phases can be expressed by the following equations:



In summarizing, it can be said that natural Black Sea sediments of this horizon contain a substantial quantity of Fe(III) as a sulfide (up to 20% in the preparation and with a concentration of 1:5 up to 4% in a real sediment). The discovery of a sulfidic compound of Fe(III) is important for diagnostic purposes, as it is an indicator of interaction of sulfidic sulfur with amorphous iron hydroxide in the sedimentary bed and, generally, an accumulation of oxidized forms of elements. Against the background of a Recent strongly reductive setting, this allows distinguishing in the sediment periods of oxidative sedimentation environments.

The current notions of the events in the Late Quarternary history of the Black Sea [8] allow the possibility of such environments during activization of glacial discharge until salinization of Black Sea waters.

For understanding the geochemical processes responsible for the origination and preservation of this phase in the sedimentary bed, we will discuss the known methods of formation of sulfide compounds of Fe(III) and characterize in some detail the sedimentation in that period.

Three variants of flow-temperature synthesis of Fe(III) sulfides have been described in the literature which differ in the chemical form of iron. In addition to the experiments with amorphous hydroxide [5] and Fe(III) alcoholates in an anhydrous medium [9] described above, a weakly alkaline solution of a tartaric complex of Fe^{3+} was subjected to hydrogen sulfide treatment [9, 11]. A natural analog of this experiment could be an interaction of bacterial hydrogen sulfide with various organocomplexes of Fe(III). Even maximum concentrations of these forms in interstitial waters of sediments, however, are so low that they could supply only trace amounts of sulfides that could not be determined analytically at present.

Another theoretical possibility of formation of these compounds is of an equally small practical significance (in qualitative terms): an interaction of certain forms of Fe(II) forms with elemental sulfur and its soluble derivatives ($\text{S}_2\text{O}_3^{2-}$, S_n^{2-}) in an alkaline medium. The contents of these sulfur forms in sediments are also very low and could not be sufficient for accumulation of significant amounts of sulfide. At the trace concentration level, however, such interactions are possible and are an important detail in the overall mechanism of diagenetic sulfide formation.

The most likely mechanism of development in natural sediments of the phase of Fe(III) sulfide identified chemically and instrumentally is probably the reaction between dissolved sulfide sulfur (HS^- , S^{2-}) and amorphous iron hydroxide; a previous accumulation of the latter in the sediments is a necessary condition for this process to occur.

Fe(III) sulfides are metastable by their chemical nature. They are a rare example of coexistence in the same solid phase of a strong reducer (S^{2-}) and an oxidized form of the element Fe(III). The redox interaction of these agents and the formation of more stable sulfide forms (FeS , FeS_2 , Fe_3S_4) evolves actively in slightly acid and neutral media in the range of pH 4.5-7.0; in an alkaline medium it is slowed down because of the following factors. All the known Fe(III) compounds that could be a source for low-temperature Fe(III) sulfides are of a coordination type, including amorphous iron hydroxide, which is a system of intensely dehydrated, disorderly, unequally polymerized coordination structure at different stages of dehydration and oleation. This state of a reagent, fully corresponding to the notion of gel in colloidal chemistry, offers a rational explanation of the mechanism of sulfide formation in terms of the chemistry of complex compounds, taking into account the effects of colloidal chemistry — the high permeability of gel to true solutions and dehydration processes determined thermodynamically and continuing up to the formation of crystal structure fragments.

Manifestations of redox properties of iron and sulfur in such a system are controlled by deformation and destruction of the coordination sphere of Fe^{3+} ion. The high coordination potential of Fe^{3+} ion, determined by its charge, electron structure, and size, provide in an alkaline medium for the formation of labile polymerization-prone anion hydroxycomplexes.

Because of the capacity of sulfidic sulfur to function as a monodentate ligand, providing simultaneously a bridge link between neighboring iron ions, an elementary act of sulfide sulfur interaction with amorphous hydroxide in these conditions represents the exchange of a hydroxyl group in the coordination sphere for sulfidic sulfur. The ligand field of the anion complex in general has a screening effect on the valent sulfur electrons, preventing their transfer to central Fe^{3+} ions; as a result, S^{2-} becomes one of the ligands of mixed hydroxysulfidic coordination compound.

A slightly acid and even neutral medium prevents the formation or causes the destruction of a saturated hydroxyl coordinate sphere of Fe^{3+} as a result of neutralization and removal of some of the hydroxyl groups. The screening effect of the anionic surrounding in this case is insufficient to stabilize the $\text{Fe}^{3+} - \text{S}^{2-}$ bond, and the interaction in such conditions involves an uninhibited redox reaction. This accounts for the exceptionally high sensitivity of the hydroxysulfidic and sulfidic compounds of Fe(III) that are formed to a drop in the pH of the water environment.

This theory is supported by a number of in vitro studies [3, 5, 6].

The sulfidization of amorphous iron hydroxide can be classified as a topochemical interaction, characterized by diffusional penetration of mobile dissolved reagent (HS^-) to the reaction center fixed in the solid phase — the coordination sphere of Fe^{3+} ion; in the case of a hydrated permeable gel particle this is associated with the relatively slow gradual entrainment of substance in the reaction. The sequence is complemented spatially, as mentioned earlier, by the sequential nature of the sulfidization of an individual coordinate structure, because the maintenance of electron equilibrium at the instant of ligand exchange, i.e., the formation of $\text{Fe}^{3+} - \text{S}^{2-}$ bond itself, is provided precisely by the presence and the influence of hydroxyl groups organized into the coordination sphere. For this reason, mixed-ligand compounds that include, along with sulfidic sulfur, hydroxyl groups will inevitably be the first reaction product. Among the individual compounds of this type, one can speak with confidence of amorphous hydroxysulfide with $\text{S}^{2-}/\text{Fe}^{3+} = 1$, which was isolated together with kan-site as H_2S (in excess), and was passed through a suspension of freshly precipitated iron hydroxide (pH 6) in a saltless environment [5]. The existence of such a phase is confirmed by the results of analysis of the preparation studied — see formula (4). It has been established experimentally that subsequent sulfidization of this intermediate product is slightly hampered and requires the presence of a significant excess of sulfidic sulfur in the solution, whereas the phase with $\text{S}^{2-}/\text{Fe}^{3+} < 1$ binds dissolved sulfur completely [5].

This suggests that at very low concentrations of sulfidic sulfur, typical for interstitial waters of natural sediments, a complete sulfidization of hydroxide gel particles does not provide entirely the stoichiometry of Fe_2S_3 sulfide but is limited to forming hydroxysulfidic compounds of a variable composition.

The analysis of the natural system from Black Sea sediments confirm this interpretation. However, there are no reasons to deny completely the possibility of fragmentary isolation of Fe_2S_3 crystal lattice from the mass of amorphous sulfidic gel as it ages, i.e., with continued dehydration and ordering. Because of their chemical instability, however, both amorphous hydroxysulfides of a variable composition and crystalline Fe_2S_3 in a sedimentary bed are susceptible to redox decay; the direction of this process is to be determined in the future depending on the conditions.

After outlining the general picture of sulfidization of amorphous iron hydroxide and the types of the resulting products, we must pinpoint in the history of the Late Quaternary Black Sea sedimentation the most likely moment of its intense deposition.

Besides the sample from Neoeuxinian hydrotroilitic sediments of the western continental slope studied (see Fig. 1, station 805), trace amounts of Fe(III) sulfide in the same mineral association have been found in deep-sea sediments of the central part of the western halistase of the sea (station 806, depth 2100 m). In the profile of the sedimentary bed, both interlayers with Fe(III) sulfide occur within the Middle-Neoeuxinian (Late Glacial) horizon enriched in hydrotroilite. Sediments of this horizon accumulated 18,000–11,000 years ago and are identified by a peculiar spore-pollen spectrum, different from those of the underlying and overlying sediments, as well as by characteristic hydrotroilitic pigmentation. Other distinctive traits are the variability of CaCO_3 and Corg composition and granulometric composition of sediments, both in plan and vertically. The accumulation time of this horizon was characterized by periodic short warmings of climate in the Late Würmian, which in general corresponds to a stabilization of the climates that preceded the end of the last glaciation. Accordingly, abrupt changes of sedimentation regimes took place, primarily with an activation of glacial discharge that periodically increased the supply of terrigenous calcium carbonate and terrigenous plant organics with the spore-pollen spectrum that reflected in the sediments the specifics of vegetation of the northern areas of the catchment basin in this clinically unstable period. Of a definitive significance for the formation of amorphous iron hydroxide, however, was an abrupt change in the basin hydrology and the resulting redox environments in the bottom water.

In the interglacial epoch the Black Sea basin had a normal oxygen regime. Over a long period of existence of a landlocked lake-sea, the subsided waters gradually became depleted of oxygen and acquired an anaerobic quality after the discontinuance of mixing and exchange with surface aerated waters and as a result of water-body stratification.

After dissolved oxygen reserve was depleted, the organic matter, in amounts determined by the relatively low biological productivity of the sea and a limited terrigenous discharge, began to be brought into the thick anaerobic zone, where, instead of oxidative decay, its transformation proceeded by way of anaerobic destruction, i.e., hydrolytic disintegration and dissolution. These processes resulted in a gradual accumulation, in the water body, of dissolved and colloiddally dispersed products of organic matter decay, which did not lose their reducing capacity, creating a reserve of biogenic elements in deep waters. The only oxidized form that brought in significant amounts into this zone was terrigenous iron hydroxide, which in anaerobic waters was to a large degree reduced, resulting in a gradual concentration of dissolved Fe(II).

After ice discharge was activated during the Middle-Neoeuxinian time, cold high-oxygen waters sank because of their great density mainly into the bottom part of the basin with an intense vertical mixing of previously stagnant stratified water masses; this resulted in a rapid oxidation of accumulated ferrous iron and deposition of layers enriched in amorphous iron hydroxide. Its preservation in the sedimentary strata (until sulfidic sulfur penetrated into this horizon by diffusion and reacted with it) is attributable to fractional avalanche deposition of hydroxide free of organic matter and a simultaneous oxidation of organic reducers. In the contact interlayers, the contents of buried organic matter was also very low.

In the course of subsequent accumulation of Late Glacial sediments, each intensification period of glacial discharge produced an aeration of deep waters and the seafloor surface. The bulk of Fe(II) had already been oxidized, so in more recent sediments one should expect the accumulation of only minor accessory amounts of amorphous Fe(OH)₃ phase, reflecting mainly the periodic pattern of coagulation of colloidal hydroxide, which became stable in the waters of desalted basins in the course of Fe(II) oxidation. This means that isolated interlayers of the sedimentary bed after sulfidization could contain impurity amounts of Fe(III) sulfides.

The existence of colloidal-disperse phase of iron hydroxide in desalted waters implies an additional possibility of its intensive massive deposition, namely coagulation at the time when Mediterranean waters broke through the Bosphorus and began to salinize the Black Sea. An abrupt increase in the content of reactive organic matter in the sediments in that case and the development on its basis of a sulfate reduction process make an accumulation of Fe(III) sulfides at that time unlikely, either because of possible earlier reduction of Fe(III) by organic reducers or because of a significant drop in pH due to interaction of sulfidic sulfate with Fe(OH)₃, that would preclude the formation of these compounds.

A further directed search for Fe(III) sulfides in hydrotroilitic Black Sea sediments is certain to clarify many details of the Neoeuxinian sedimentation. There is a need for developing methodologies that would allow identifying chemically microscopic amounts of amorphous Fe(III) sulfides mixed with other sulfidic phases. Another aspect of this problem is the fact that the capacity of Fe(III) sulfides for intraphase decay with the formation of greigite endows this relatively widespread mineral with the function of an indicator of redox settings.

The study has thus shown that it would be promising to investigate the phase composition of marine sulfidic sediments with the set of methods described in the paper; despite the complexity and instability of low-temperature sulfidic systems, with these methods it is possible to detect individual crystalline or amorphous phases, observe their transformations, and in general shed light on the interactions of sedimentation and diagenesis processes.

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